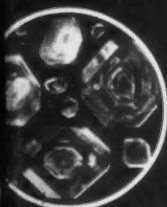
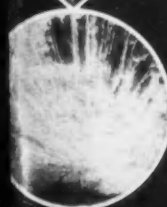
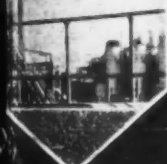


CHEMISTRY



NOVEMBER
1948



Plentiful Glycerine	1
Glycerine Synthesis	5
Research and Industry	7
Classic of Chemistry:	
Discovery of Glycerine	13
Real Quartz Crystals Grown	16
Magnetic Particle Predicted	19
Xerography Dry Photo Process	20
For the Home Lab: Fireworks!	22
Three Nobel Prize Winners:	24
Medicine—Paul Mueller, DDT	
Physics—P. M. S. Blackett, Cosmic Radiation	
Chemistry—Arne Tiselius, Electrophoresis	
Patents in Chemical Fields	28
The Atomic Nucleus	31
New Tests for Paints	37
The Strange Behavior of Rubber	40

Editorial:

Peace and Destruction
Inside Front Cover

25¢

Peace and Destruction

► It is an interesting coincidence that a method for making glycerine more abundant comes out so close to the announcement of this year's Nobel prizes. Nitroglycerine was the foundation of Alfred Nobel's fortune and of his great fear. He had first-hand experience to intensify his fear of the explosive he had made "safe." One of his brothers was killed in an explosion in the plant where dynamite was made.

Alfred Nobel was one of a series, coming down now to the scientists who developed the atomic bomb, of technical men who fear the use to which their inventions can be applied. They do not feel guilty about the inventions as such. They know that the development of the art, to which each of them contributed his small share, was continuous, necessary and inevitable. The long-time result, whether it is improvement of mining and engineering methods through dynamite or improvement of our understanding of matter through nuclear and isotope study, is good. But the technical man, with his long-range vision, is baffled by the preoccupation of his neighbors with tools of murder.

Many remedies have been suggested to rid the human race of its urge to kill itself off. Some, mistaking the means for the impulse, propose a vacation from scientific advances until the world learns to use wisely those that have already been made. That is like suggesting that the human race would be better off if there were no babies for a hundred years. It would solve some problems, certainly, but the final result would be something quite different from a solution of the original difficulty.

Nobel's solution was to dedicate his fortune to encouragement of science and the arts of peace. This has rewarded, and perhaps stimulated, those whose faces were already set in that direction. Perhaps some day, as a by-product of a sufficiently horrible invention, the way to peace will be discovered.

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► **SYNTHETIC GLYCERINE** plant at Houston, Texas, where a new process for obtaining this important chemical from a source other than fat has just been put into operation on a full commercial scale.

Plentiful Glycerine

by HELEN M. DAVIS

► **BY-PRODUCTS** for which the demand outgrows the source of supply can provide an embarrassing bottle-neck in industry. They can also provide a challenge to the synthetic chemist, who is supposed to be able to turn out the desired chemical product from almost any raw material available.

The trick is not always easy, and

the Shell Development Co. is proudly announcing their solution to a particularly acute problem of the sort. For the century and a half since glycerine was isolated, and for some undetermined number of years before that, glycerine has been made as the by-product of soap, which is made from fats and oils.

These naturally occurring substances are glycerides of fatty acids. A metallic

salt of a fatty acid is a soap, whether it is the soft and easily soluble sodium or potassium compound used for washing, or the insoluble soap formed by lead or other heavy metal. In soap making, the metal is introduced as the hydroxide, and after the soap separates the hydroxyl ions combine with the glyceride part of the fat molecule to form glycerine, which is a trihydric alcohol.

For a long time soap making provided all the glycerine needed, and other methods of manufacture were not considered. But the clear, thick, sweet liquid proved useful for more and more purposes, and the supply of fat began to run short. Detergents could take the place of soap, but there is no satisfactory substitute for glycerine. Some other source for it had to be found.

Chemists of the Shell Development Company tackled the problem, in order to find out whether the hydrocarbons flowing from oil wells could be remodeled into the kind of carbon compound which is glycerine. There are two parts to a problem tackled in this way by a commercial research laboratory—first, to find out whether it can be done at all, second, to adapt a successful laboratory method to large-scale handling of materials flowing continuously through pipe-lines. A third, and all important, phase of the problem then comes into view: the costs of the materials and of the energy necessary to carry on the process, in relation to the price at which the finished material can be delivered to the user.

There had really never been but one way to make glycerine before. The Swedish chemist, Scheele, who first

identified the substance in 1783, made it out of olive oil, and a number of other oils, hydrolyzed with lead oxide. Housewives, who had been throwing glycerine away in the waste liquor for centuries, made their soap out of beef tallow, hydrolyzed with lye leached out of wood ashes. Commercial producers induced live steam to substitute for alkalies in splitting the fats. But chemically these processes all use the same principle. Shell research chemists wanted to make glycerine without bringing in the fatty acid radicle at all.

They found the answer in chlorine, which is a convenient element to use in rearranging organic compounds, because it unites with them readily. Not only that, but it is willing to switch partners, or even to help introduce two carbon-containing radicles and then step gracefully out of the picture. In this case, the chemists asked chlorine to substitute for hydrogen in propylene, a gas they could start with.

At first chlorine accepted the invitation to join with propylene all too willingly, producing a compound which would not go on to form glycerine. The chemists wanted it to react more moderately, so that one chlorine atom would substitute for one hydrogen, without disturbing the rest of the structure. It is axiomatic in chemistry that a series of reactions which will run in one direction under ordinary conditions will often reverse itself when the conditions are changed. Heating material up will make it do one thing, cooling it down will make it do the reverse. Putting on pressure will produce a different effect from pumping out the air. And the concentrations of the reacting substances have an enormous effect on what kind of

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finished material runs out of the pipe at the end. The research chemists decided to see what varying the conditions would do for their problem.

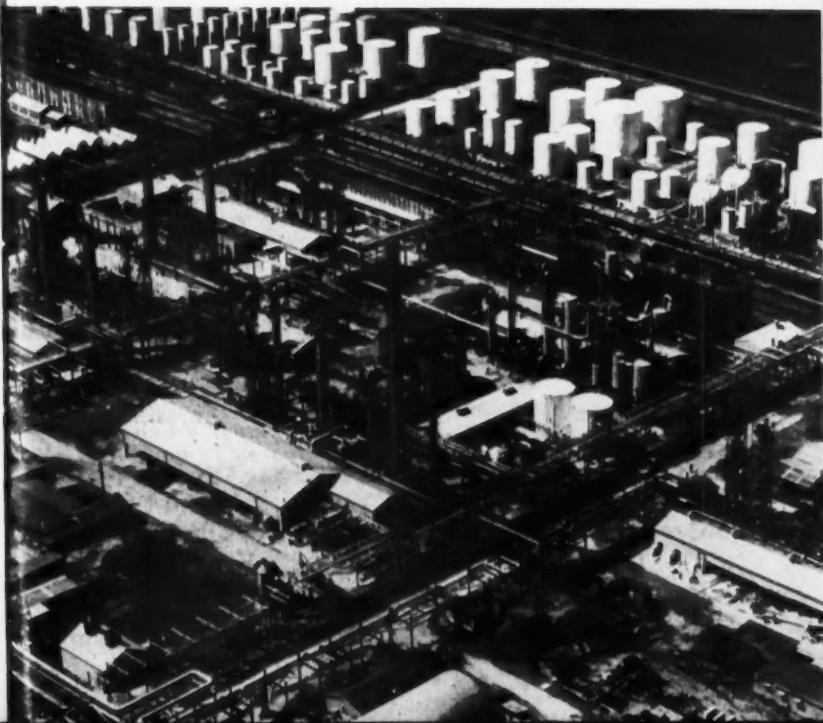
The immediate necessity was to turn propylene into a similar compound, named allyl chloride, by substituting one chlorine for one hydrogen atom in the molecule. To learn how to do this, in the necessary quantity, was the object of their long series of experiments, for they already knew how to turn allyl chloride into glycerine. Their outline of the process follows this ar-

ticle, with structural diagrams which make clear the essential steps.

The synthetic process takes glycerine out of the by-product class, so that its supply need no longer be dependent on hoarded scraps from housewives' kitchens. A more than even exchange can now come back to those kitchens in mayonnaise, bakery products, flavoring extracts, candy and soft drinks, for glycerine is that rarity among chemicals, a harmless compound that tastes good!

Although a major use is still for

► *THE CHEMICAL PLANT of the Shell Oil Co. at Houston, Texas. The distinctive group of towers of the synthetic glycerine section may be recognized near the center of the picture.*



nitroglycerine, which Alfred Nobel tamed as dynamite, glycerine is used in a constantly growing list of other products, notable among which are cellophane, paint and tobacco. Thick and slow-moving without being sticky, its viscosity and ability to mix with

water allow glycerine to give a pleasing texture to many products from cosmetics and creams to printing rollers and glue, not to mention the sparkling tear that trembles so realistically on the movie queen's synthetic eyelash.

► THE STRUCTURAL FORMULAS below and on page 6 illustrate the similarities in structure between the source chemicals and glycerine, the desired goal. On the opposite page, Shell chemists tell of their problems in getting the atoms to combine in just the right configuration.

Figure 1



Figure 2

Allyl Chloride

Chlorine

Trichloropropane

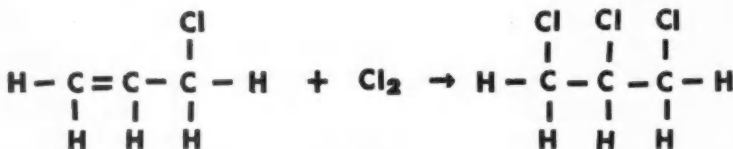


Figure 3

Glycerol Monochlorohydrin

Glycerine



Structural Diagrams Show Hydrocarbon Rearrangement

Glycerine Synthesis

An account by the Shell Development Company describing the essentials of the process by which they have succeeded in making glycerine on the production line. "It is not meant," they say, "to be a complete report of this huge research project, but only a condensed and formalized story of some of its significant aspects."

► THE PROBLEM of synthesizing glycerine had engaged the thinking of research workers, both academic and industrial, for many years. Through their work a number of processes had been developed which appeared to be applicable to commercial use. The first and most promising was a process which used trichloropropane, a material quite similar to glycerine in structure. A comparison of these two chemicals is shown in Figure 1.

Trichloropropane can be made by adding chlorine to another compound called allyl chloride, in the reaction shown in Figure 2.

It was also known that glycerine could be produced by means of a group of chemicals known as chlorohydrins, which, like trichloropropane, are also quite similar to glycerine. A comparison of a typical chlorohydrin with glycerine is shown in Figure 3.

Chlorohydrins of the sort shown in Figure 3 can also be made by the use of allyl chloride.

With these facts at hand, it became obvious that the real key to glycerine synthesis was not making glycerine itself, but making allyl chloride, the

stepping stone to glycerine. This problem had already been approached by Shell scientists in a series of experiments with propylene, a hydrocarbon gas produced in large quantities during petroleum refining.

The structure of propylene is very similar to that of allyl chloride. The only difference is seen on the third carbon where propylene has a hydrogen atom and allyl chloride has a chlorine atom. Figure 4 shows a comparison of these two chemicals.

To the uninitiated it might look easy to simply substitute a chlorine atom for the hydrogen atom, and thus make allyl chloride. But actually, when chlorine was reacted with propylene, the chlorine simply added on to what was already there, as shown in Figure 5.

This reaction produced a material that was worthless for glycerine synthesis. But the problem would be solved if the chlorine atom could be made to *substitute* itself for the hydrogen instead of just adding on to the other carbon atoms.

Advanced thinking of the time indicated that this was probably not possible and the scientists realized that in trying to produce the reaction they were moving in an entirely new direction. However, one approach—that of carefully controlling the reaction conditions—looked promising and they decided to try it.

Months of laboratory work followed. Hundreds of different experiments

Propylene

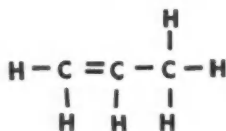
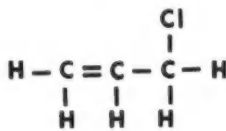


Figure 4

Allyl Chloride



Propylene

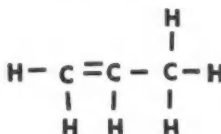


Figure 5

Chlorine

Propylene Dichloride

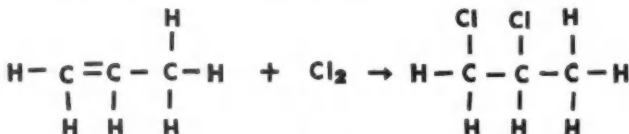
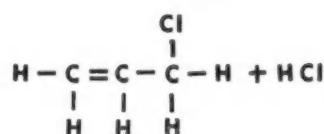
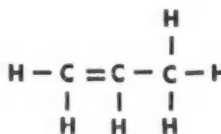


Figure 6

Chlorine

Allyl Chloride



were made till, at last, they found the conditions that would produce allyl chloride in commercially significant yields. In diagram it looks so simple that it's hard to believe it has been acclaimed by scientists as one of the greatest contributions to organic chem-

istry. Figure 6 shows this all important reaction.

This was the culmination of more than a hundred years of scientific research . . . a key to a method of glycerine synthesis adaptable to operation on a commercial scale!

On the Back Cover

► INITIAL CONCENTRATION and desalting of synthetic glycerine takes place in this tank atop a tall tower.

Genuine amber can be readily distinguished from certain imitations by floating in water; it is heavy enough to sink in pure water but light enough to float in brine.

**Co-operation is the Keynote
Of Modern Industrial Research**

Research and Industry

by DR. W. V. HOUSTON

President, Rice Institute, Houston, Texas.

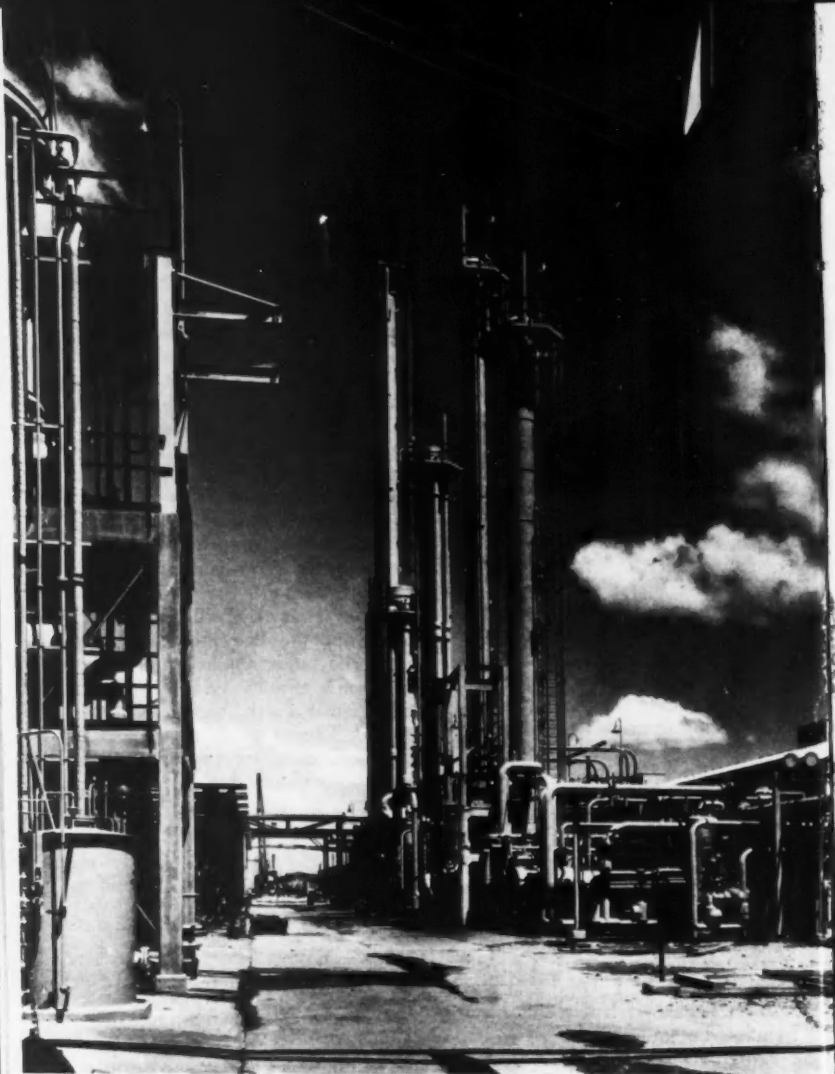
Address at the dedication of the new synthetic glycerine plant in Houston.

► TO AN EVEN greater extent than some other industries, a chemical plant is an outgrowth of scientific research, and depends on research for its future. As you all know, the research laboratories of the Shell Company are very extensive. The executives of the Shell Companies have shown themselves exceedingly research minded, in a research minded industry.

As a matter of fact, the word "research" is very popular everywhere. It is so popular that sometimes the use of the word tends to outrun the facts behind it. Children in school are told they are doing research when they go to the library to look up a fact. The advertisements are full of references to research, sometimes accompanied by beautiful pictures of scholarly looking men in long white coats, surrounded by a maze of glassware and blinking colored lights. The authors of short stories are apt to characterize the hero, formerly a struggling artist, as a research chemist, or even a physicist, on the verge of a world shaking discovery. The research scientist, once a harmless but mildly eccentric individual, has now become either a threat to the world, or its principal hope.

As is often the case, the popular view is a caricature, an exaggeration. But behind the caricature lies a vital

reality. The recognition of this fact is evidenced by the money now being invested in research work both by industry and by the government. Within the past ten years there has been a significant change in the administrative problems of a research group. Ten years ago the difficulty was to persuade those with the responsibility of allocating funds to provide enough for research. Highly competent and capable scientists were handicapped by inadequate assistance and inadequate equipment. Today the situation tends to be the opposite. Both industrial and government funds are being poured into research at such a rate that the limiting factor is a shortage of trained personnel. This creates other problems of administration, for nowhere is it easier to waste money than in this kind of activity. A research man, lacking insight and imagination, can spend just as much money, if not more, than a man of genius; and I sometimes fear that the present high regard in which research is held may eventually suffer from too lavish an expenditure of funds in the wrong places. It takes a long time to train an independent research man. It takes a minimum of seven years for college and graduate study, before a man is ready to begin, and this process cannot be hurried very much. The principal problem facing the research directors of the country today is that of recruiting and



► *THIS CLUSTER of towers contains the processes of propylene preparation and allyl chloride synthesis, steps in the manufacture of glycerine from petroleum products.*

training the men who will be the scientists of the future.

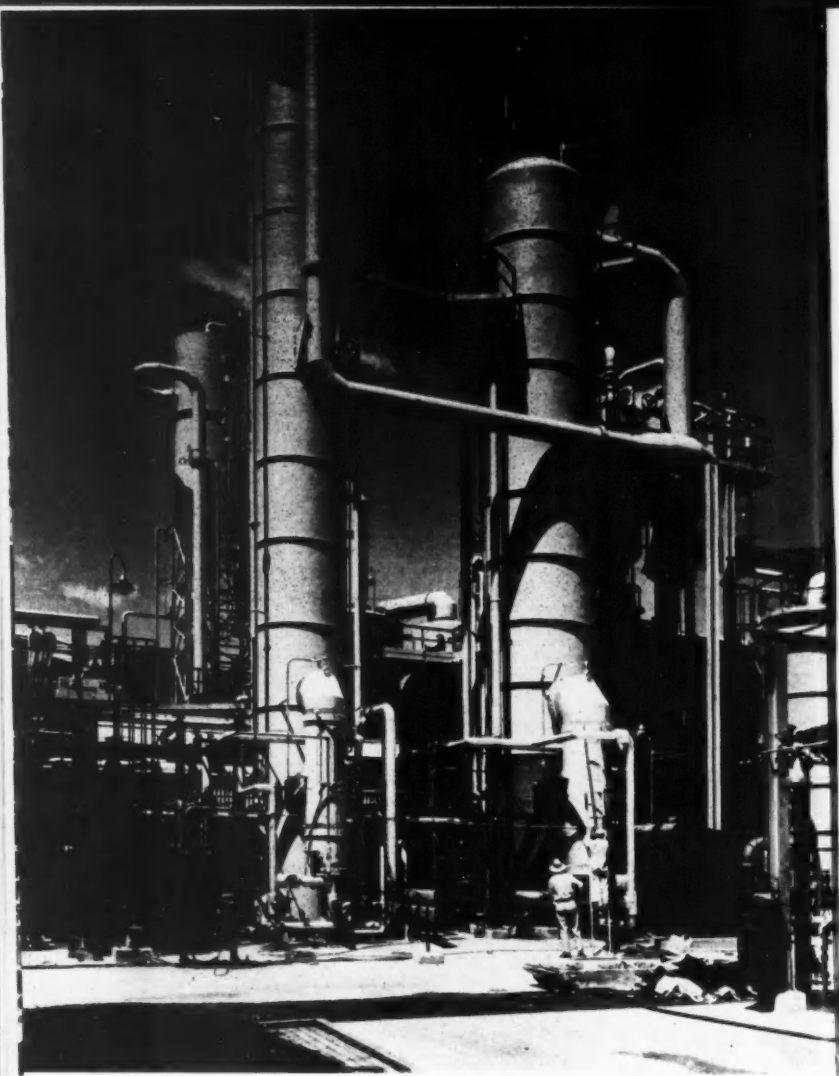
In the early days of the industrial revolution an industry frequently centered around one individual, an ingenious inventor. Sometimes he was able to develop and market his own invention. Sometimes he was not. But often a factory depended upon some sort of a trade secret which was the product of one man's brain. The lonely inventor, fearful for the security of his idea, often at the mercy of the financiers, has become a popular character of fiction, but at present pretty much out of date.

At a later stage there developed engineering departments where the details of machinery and devices were worked out according to well established practices. These required men trained in engineering practice, skilled in manufacturing methods, and practitioners of the art, rather than the sciences of engineering. But these eventually proved inadequate for the rapid development of new products. Today research departments have taken over the job of looking into the future. One often wonders what it is about a research department that makes it so valuable. What mysterious power does such a group have that enables it to justify its budget?

It seems to me that the principal characteristic of an industrial research organization is its ability to bring together a variety of skills, experience, and knowledge, and to apply them to the problem in hand. A one-man research department is almost an anomaly. Only very rarely can one man have at his command the wide variety of detailed knowledge necessary. For in addition to being wide, the knowl-

edge must be deep. The state of our technical development is now such that the obvious scientific facts have been pretty well exploited. A man with average training can probably make adequate use of the force of gravity on the surface of the earth, but he might never have heard of the coriolis force that tends to deflect projectiles because of the earth's rotation. An average electrical engineer will understand how to transmit electrical power along a circuit of two wires, but he might not understand how to transmit it down the inside of a hollow tube. The training of the research man must be a profound training, for he is expected to devise new things, to make new applications of laws of science. He must know his science thoroughly and deeply; a mere superficial acquaintance is not enough.

But what is this science? What is it that a research man in industry must know? One definition of science, old enough to be respectable and included in dictionaries, and short enough to be remembered in spite of being only partly correct, is that science is classified knowledge. Insofar as this definition is adequate, the emphasis is on the classification. The mark of a science in an advanced stage of development is the brevity and conciseness with which its laws can be stated. Newton's laws of motion combined with his law of gravitation describe the whole of classical positional astronomy, and yet they can be stated in a few paragraphs. The laws of thermodynamics are only three in number and can be written on a page. All the laws of electricity and magnetism are included in Maxwell's equations. On the other hand, the field of nuclear



➤ DWARFED by the maze of pipe lines and reaction towers, two men adjust a detail of synthetic glycerine production and provide the scale of measurement for this huge set-up of chemical apparatus.

physics is less developed. Much of it consists in a tabulation of facts that have been discovered, but not yet satisfactorily organized. The so-called social sciences show their primitive state in just this way. They include a great deal of fact, more opinion, but very little generalization into simple and concise laws upon which everyone is agreed.

But whence comes this science? Who makes these generalizations? Who classifies the knowledge? Traditionally science grows in the universities. It is in the atmosphere of a university, where one is not trying to solve a particular problem, but is trying to formulate his knowledge in the best way for understanding and for presentation to others, that this kind of classification is most naturally made.

Of course such work is not confined to universities. Particularly in recent years, when many applications have already drawn to the limit on the available science, industries and government have undertaken this kind of work. I was told a few weeks ago by a well known university chemist that he believed the Shell Company was perhaps the leader among industries in the prosecution of this kind of fundamental research. Government laboratories, also, see the necessity for enlarging the storehouse of basic organized knowledge upon which they can draw when needed. But it seems to me still, that the universities will remain the most appropriate places, and the most effective places, in which such work can be done. In an industrial laboratory, practical problems will always be pressing for solution. The urgency of this year's demands will strongly tend to outweigh the possi-

bility of needs five years from now, and the general approval of the man who removes a troublesome difficulty will usually outweigh that given for the formulation of a law which few persons will bother to understand until it is needed. The development of science itself can be carried on in an industrial laboratory, but with difficulty.

In a university, on the other hand, the atmosphere is conducive to the formulation of general laws. Every day the professor must organize his knowledge for presentation to a class. Every day he must try to describe some field of science so it can be understood by those less acquainted with it than he is. Every day he discusses with fresh and inquiring students the problems of science. Such an atmosphere is more conducive to the growth and development of the science itself.

And so I believe the universities contribute to industry in general, and to the chemical industry in particular, in two ways, by education and by research. The men who will carry on the technical side of the industry, as well as those responsible for the organization, will need a university training. Speaking particularly of the technical side, they will need an intensive and extensive university education; for as you know, industry is coming to recognize more and more the advantages of the training ordinarily denoted by the doctor's degree. Not many decades ago the management of industry was a little hesitant about taking into its organization men who might turn out to be long haired eccentrics. They felt that practical common sense and the ability to get things done was more important than

any profound understanding such men might have of some of the remoter aspects of science.

The situation is a little different now. In the first place, many of the scientists have had their hair cut. They have learned that there is no merit in being different. They must work with other people, and they have been able to demonstrate about the same average amount of common sense as possessed by anyone else. In the second place, the industrial problems of today are no longer as simple as they once were. The direct application of well known laws is no longer adequate. Often the pertinent laws are not well

known, perhaps not known at all. The only men who can deal effectively with such situations are those with the most complete possible training, and an understanding of the research spirit.

The other way in which universities contribute to industry, is in their own prosecution of fundamental research work. This is not, in general, work leading to patentable ideas. It is not usually directed toward the solution of practical problems. But it is the steady development of the sciences upon which industries, such as this, ultimately depend; and it is a matter of great importance to our industrial civilization.

Hydraulic Fluids Safe From Fire

► **NON-COMBUSTIBLE** hydraulic fluids with a water base, for use in aircraft, will not burn and are said to be the first successful non-inflammable hydraulic fluids ever made.

These Hydrolube fluids, announced by the Navy, where used in landing gear, brake and flap control hydraulic systems, will eliminate fire hazards if high-pressure hydraulic lines are ripped open by bullets or shrapnel. The material will be of value in both military and civilian airplanes by lessening danger in emergency landings when hydraulic lines are sometimes ruptured.

Hydrolube fluids, replacing combustible petroleum-base materials, have been thoroughly tested in Navy planes during the past two years. They are now being tested by the Civil Aeronautics Administration for commercial airplane use. They contain, in ad-

dition to the water, an anti-freeze, a thickener, corrosion inhibitors, a wear preventive, and an organic chemical to make all the ingredients soluble.

Ethylene glycol is used as the anti-freeze. A special polymer is added to the water and glycol to increase the thickness. In addition to not burning, the material has a freezing point 82 degrees Fahrenheit below that of water, is much less corrosive than water, has greater freedom from packing deterioration and leakage than present hydraulic fluids, and has satisfactory lubricating qualities.

Hydrolube was developed in the Naval Research Laboratory by Dr. W. A. Zisman and assistants. In parts of the development, the laboratory had help from the DuPont Company, Wilmington, Del., and the Carbide and Carbon Chemicals Corporation of New York.

**You Can Repeat These
Historic Experiments**

The Discovery of Glycerine

A Classic of Chemistry

Scheele was a first-rate chemist, in spite of having his head full of theories about explaining all phenomena by presence or absence of "phlogiston." The translator of his papers has to some extent modernized the language, for, in the eighteenth century, chemists tended to create their own technical terms as they went along. The present-day student should have no difficulty with those here. Litharge, which is the yellow oxide of lead, PbO, still goes commonly by that name. Vitriol persists in literature as the name for sulfuric acid, and acid of nitre is obvious. Spirit of wine can, of course, be nothing but ethyl alcohol. Scheele's alkaline tincture was probably an alcoholic solution of potassium tartrate. Trituration is the process of grinding in a mortar. Empyreumatic matter comes from the breakdown of the carbon compound when subjected to too high heat, and is the reason that distillation of glycerine is today carried out under reduced pressure.—EDITOR'S NOTE.

THE COLLECTED PAPERS OF CARL WILHELM SCHEELÉ, *Translated from the Swedish and German Originals by Leonard Dobbin*, London: G. Bell & Sons, Ltd., 1931.

Experiments relating to the Peculiar Saccharine Principle in Expressed Oils and Fats. V.N.H. 4 (1783), 324-329.

➤ IT IS PROBABLY still unknown that all fats and expressed oils are endowed by nature with a sweet substance that is distinguished by its special behaviour and properties from the generally known saccharine principles which the vegetable kingdom produces. This sweet substance shows itself when these oils are boiled with calx of lead and water; for there is then produced a hard mass which is known in apothecaries' shops under the name of *em-plastrum simplex*. This plaster is a species of soap which, although it can-

not be dissolved in water, is nevertheless soluble in part in strong spirit of wine by aid of trituration.

The actual method to obtain this sweet substance is this: one part of finely pulverized calx of lead, or litharge, is boiled with two parts of fresh olive oil and one part of water, during continuous stirring with a spatula, until all the calx of lead is dissolved by the oil; then one part of water is again added and it is boiled anew for a couple of minutes, after which the boiler is taken from the fire and set aside. When the plaster has cooled, the water which lies above it and which contains the sweet substance, is poured off: this water is filtered and is boiled down until the residue becomes as thick as syrup.

As calx of lead communicates to certain acids a sweet taste, it is not remarkable to hit upon the idea that

some acid in the oil has attacked the calx of lead, from which this sweet substance might then be derived. Such calx of lead should, however, then be precipitated again by the addition of alkalies or of acid of vitriol, but no precipitation takes place so long as the oil has not become old and rancid, because this sweet substance then contains a little calx of lead, which, however, can be separated from it by means of a careful and just sufficient addition of acid of vitriol.

Other Oils

Before I proceed to describe the nature of this sweet substance, I shall cite the further experiments which I made with various kinds of fatty oils, and their behaviour with calx of lead. I boiled fresh oil of almonds with litharge and water according to the above-mentioned method. The result was the same, for the sweet substance which I obtained could not be distinguished from that which olive oil yields. The state of matters was similar with rape oil, even linseed oil gave me the same result. I likewise boiled litharge with the oil which is separated from soap by means of acids, whereby I got a similar sweet substance. It is to be noted, however, that this mixture had scarcely entered into ebullition before the consistence of plaster was already attained. The question now arises: Whether also the same oil, after it has once united with calx of lead and, consequently, has given up its sweet substance, can give more of a similar sweet principle when again treated with calx of lead in the same manner? To separate the oil from the dissolved calx of lead, or simple plaster, is not so easy to accomplish as to separate it from soap, because such a mass cannot

be dissolved in water and only to a small extent in spirit of wine; nevertheless this can be done by means of affinity. The plaster is cut into small pieces, which are dissolved by trituration in a glass mortar with a mixture of eight parts of the most highly rectified spirit of wine and two parts of concentrated acid of vitriol. The acid here unites with the calx of lead and the spirit of wine with the oil. This solution is poured upon a filter and eight parts of water are mixed with one part of the filtered liquor, when the oil separates and floats on the top. I now mixed this oil with ground litharge and water, which mixture happened, by chance, to stand till the following day, when I found it during this time to have assumed the consistence of plaster, without heat. I evaporated the water which I poured off from this mass till at last a few drops, with a sweetish taste, remained. Hence the oil united with calx of lead still contains some sweet matter, though in smaller quantity, since the same quantity of olive oil yields about twelve times more of this sweet substance. Hereupon I examined the behaviour of milk fat, or butter, with calx of lead. The calx dissolved very rapidly, the butter became hard like plaster, and here also I obtained the same sweet substance. I now boiled fresh hog's lard with this calx and the result was the same.

Nature and Properties

Concerning the nature and properties of this sweet substance, I examined it, 1st, by the method of crystallization: I evaporated it to a proper consistence and although it stood several months in a cold place, still no crystals were formed.

2. I poured a little of this thick material upon a tea saucer and placed it upon red-hot charcoal, when the vapour took fire and the substance burned with a blue sulphur flame and left a light charcoal behind.

3. Its behaviour in the method by distillation is remarkable. Pure water goes over first, whereupon the boiling slackens and although the fire is increased no more will go over; but when the retort becomes almost red-hot, the syrup enters anew into ebullition and the receiver becomes filled with vapour which afterwards collects again in drops. It is thick like syrup, and retains its sweet taste, although it is mixed with some empyreumatic matter, like spirit of tartar. When the heat is at last increased till the bottom of the retort is red-hot, the receiver becomes filled with a brown vapour which, after it has condensed, yields a black oil with some black liquid of a bitter taste and very penetrating smell. The residuum in the retort was a light shining charcoal which did not contain any traces of lead.

4. I mixed one part of this syrup with four parts of water and placed it in a luke-warm position where it remained for several months; but the mixture had not undergone any fermentation or any other change during this time; neither was tincture of litmus changed by it.

5. To ascertain what the acid of nitre would do to it I mixed this syrup with three times as much of this acid and distilled it again therefrom; and,

as the acid became much phlogisticated by this method, I abstracted the same quantity several times, yet so that each time pure acid of nitre was taken; when eventually, after the ninth distillation, what was left behind in the retort completely thickened to a considerable quantity of crystals which behaved like common acid of sugar.

6. I mixed this sweet substance into an alkaline tincture (*tinct. tartari*) whereby no visible change occurred; but if, on the contrary, such a tincture is mixed with sugar syrup, or honey, the sugar attracts the dissolved alkali from the spirit of wine and falls with it to the bottom as a stiff mucilage.

Differs From Sugar

Hence it is seen from this that all fatty oils contain a sweet substance which differs from sugar and honey in these respects: (1) That it cannot be brought to crystallization. (2) That the sweet substance can not only withstand much stronger heat before it is destroyed, but also that it passes over into the receiver in part unchanged, with retention of its sweetness. (3) That it cannot enter into any fermentation, and (4) That it mixes with spirituous alkaline solutions. All these special differences appear to arise from a great quantity of phlogistic material which this sweet substance from fat contains, as is proved by the great amount of acid of nitre that is required for its dephlogistication before the acid of sugar shows itself; because much less acid of nitre is required for ordinary sugar.

Ultra-pure fine iron rod, 99.99% pure, obtained by electrolysis and then by cooking in hydrogen in a high-frequency radio-wave furnace, is used for comparative purposes in the spectrographic examination of commercial iron.

High Temperature and Pressure in Steel Bomb Produces Synthetic Piezo Substance

Real Quartz Crystals Grown

► CLEAR, SPARKLING crystals of real quartz, identical in every way to those produced only by the processes of nature, are being grown inside bomb-like, steel "test tubes" by a group of scientists at Bell Telephone Laboratories.

Recent experiments have been so successful that commercial manufacture of the useful mineral seems possible for the near future, it was stated by Ernest Buehler and Alfred C. Walker, at the International Union of Crystallography at Harvard University.

Starting with a small seed plate, suspended in a specially constructed bomb and subjected to unusually high temperatures and pressures, a clear crystal more than an inch long can be grown in a month.

Such crystals are not a substitute; they are the real things, with a composition identical to the quartz crystals found in nature. The only difference is that they are synthetically produced. Due to the controlled uniformity of such production, the synthetically produced crystals are superior to natural ones.

The standard growth rate achieved is four times that of any previously reported. Much greater growth rates have been obtained, but not by methods which can be successfully duplicated under controlled conditions.

Natural quartz crystals and their synthetic cousin, known as EDT, ethylene diamine tartrate, created by

Bell Laboratories, are widely used in telephone communication. Both the real and synthetic product are piezoelectric, which means that they can convert mechanical energy to electrical energy or vice versa. When electrical current is applied to them, they vibrate at certain specific frequencies. In telephony, this property is used in sending many conversations over the same channel at one time. A different crystal filter guides each conversation and keeps it from becoming tangled with all the others. Quartz is also used extensively in maintaining frequency standards in radio.

One of the first effective approaches to the problem of growing quartz was made shortly after the turn of the century by Giorgio Spezia, in Italy, who obtained crystal growth rates of about a half-inch in six months. During World War II, a German geologist, Prof. Richard Nacken, succeeded in obtaining somewhat higher growth rates.

At Bell Laboratories and other research centers in this country, studies of the Nacken process have revealed serious limitations of his method, but at the same time, uncovered new approaches.

The basic methods used are in many respects like those developed for growing the water-soluble EDT crystals. The growth rates, even those obtained early in the research, have

been higher than those established for EDT.

The material from which the quartz crystals are grown is a finely powdered form of silica, a common chemical compound which looks something like granulated sugar. This is placed in the bottom of the steel bomb and an aqueous alkaline solution is added. The seed plate, a thin wafer of quartz, is suspended at the

top of the bomb; the bomb is then sealed and placed in a furnace.

Under pressures exceeding 15,000 pounds per square inch and at temperatures of about 750 F., the silica dissolves. In its dissolved state, it rises to the cooler part of the bomb and is deposited on the seed plate, molecule upon molecule, in perfectly regular order until all of it is in the form of a single clear crystal.

Cresylic Acid Versatile

► CRESYLIC ACID, a coal tar chemical which a generation ago was used only to kill bedbugs, is now finding so many new uses in industry that a critical shortage of the compound has developed.

The shortage is so pronounced that petroleum chemicals are being utilized to supplement the cresylic acid obtained from coal tar. Dr. Sidney A. Savitt of the M. W. Kellogg Company, New York, and Dr. Robert S. Aries of the Polytechnic Institute of Brooklyn told the American Chemical Society's paint, varnish, and plastics division.

At present the petroleum industry produces about 30 per cent of the entire cresylic acid output and is endeavoring to increase this volume.

One of the biggest uses of cresylic acids is in the plastics industry, whose output is expanding very rapidly. Of the billion pound production of finished plastics in this country, about a fifth use phenol, cresoles, cresylic acids and higher boiling phenols. Cresylic acids are especially useful in moldings, lamination, coatings of textiles, and adhesives.

In addition to a domestic production of 26 million pounds of cresylic acids, this country has found such a large need for them that about 20 million pounds are imported, primarily from England. Another large use of cresylic acid is in ore flotation. With the continual impoverishing of the ores mined in this country, we need more and more agents which will beneficiate the ore so that it can be extracted economically. Luckily, cresylic acid has been found to be a good agent for the manufacture of a large number of ore flotation chemicals, and about 10 per cent of its output now goes into this field.

Textiles, medicinals, dyes, and inks consume another 10 per cent of the cresylic acid. Although 30 per cent of the cresylic acid is made from petroleum, much of that goes back into the field, as cresylic acid is used in the refining of petroleum for the manufacture of specialty oils and greases. Thus the petroleum industry contributes to some extent to its own raw materials. Cresylic acid is used to inhibit gum formation in cracked

gasolines and as a selective solvent in the purification of these gasolines.

Even though bug killing was its only use a generation ago, no cresylic acid is used for that purpose at present. However, the general field of disinfectants and insecticides consumes about 10 per cent of the cresylic acid, which is a bactericidal agent and can disinfect chicken houses, stables, warehouses, and the like.

In research at the Polytechnic Institute of Brooklyn on the manufac-

ture of synthetic cresylic acids, a new base has been found in toluene, another by-product of both coal tar distillation and petroleum refining. Toluene is converted into a mixture of cresylic acids by means of sulfonation followed by caustic fusion.

Toluene is one of the very few chemicals which is in ample supply at present, since its main use is in the production of TNT, or trinitrotoluene, which is the basis for smokeless powder. During the war, this country expanded its capacity for TNT enormously.

Industrial Advances of Future

► HINTS OF industrial advances for the future are contained in the annual report of Dr. E. R. Weidlein, director of the Mellon Institute of Industrial Research, Pittsburgh. Some forthcoming developments from research are:

Water for fighting fires will be improved by addition of chemicals that make the water wetter and therefore more penetrating and more effectively quenching.

Paint capable of standing much more heat than ordinary coatings will be made from organosilicon resins made from sand and petroleum.

Baking of bread will be improved and cheapened by using the surface characteristics of an organosilicon resin.

A new resin putty will be used to fill weld and rivet depressions in airplane wings to improve their aerodynamic efficiency.

Bentonite, a plentiful clay material, will be the basis of new compounds of industrial use.

Dirt removed from clothing in dry-cleaning will be collected from the solvent electrostatically.

Molded wood fiber of low density will be used as parts of packing containers.

Protein from soybeans will make adhesives, emulsifying agents, film-forming materials, leather finishes, paper coatings and floor waxes.

A new synthetic granular adsorbent superior to bone black for glucose and dextrose refining will be introduced.

A corn chemical, sodium phytate, will be utilized in water softening, rustproofing and textile conditioning.

A new method of disposing of the waste liquor from pickling steel will be introduced.

Experimental treatment of mental disease with porphyrin compounds will be undertaken.

Waste materials from the manufacture of glass will be used as filler in plastic, asphaltic and rubber products.

**New Subnuclear Particle Foreseen
By Noted British Physicist**

Magnetic Particle Predicted

► A NEW SUBNUCLEAR particle, this one bearing a magnetic charge instead of the more familiar plus or minus electrical charge of the proton or electron, has been predicted.

The new particle has yet to be observed in the laboratory, since its generation by an artificial atomic collision would require energies greater than provided by any present atom smashers. Neither has it been observed in cosmic ray studies, probably because no one was looking for it.

The description of the new magnetic particle, in a very technical article in *The Physical Review*, comes from Dr. P. A. M. Dirac, the British mathematical physicist now working at the Institute for Advanced Study at Princeton University.

Prof. Dirac once before, in 1931, predicted the existence of and properties for an unknown particle. That particle was the positron, and it was then actually discovered about a year later in a cloud chamber photograph by Dr. Carl D. Anderson of the California Institute of Technology.

Why add a new particle to the present long list, especially when the particles now known are so incompletely explained? Prof. Dirac answered by saying that the new particle is needed for theoretical reasons. It is needed, he said, in order to help explain why all electrons carry the same unit amount of negative charge. That electric charges, such as those on the

electron, proton or meson, do occur in even multiples of the same electronic unit charge has been known experimentally for a long time. Still, there has been no adequate explanation of this even-multiple type of regularity.

Prof. Dirac now surmises that there is no explanation for the regularity apart from the existence of magnetic particles on the subatomic level. Moreover, if there exists even one of these particles in the universe, this theory requires all electric charges to be even multiples of the electronic charge.

The particle could be created in an artificial collision having an energy of 500,000,000 electron volts, it is estimated. This puts it out of range of even the 184-inch cyclotron at Berkeley, Calif., with its 400,000,000 electron-volt particles, which artificially created mesons. Thus, for the moment, search for such a magnetic particle will have to be made through cosmic ray studies, until the billion-volt generators are completed.

What will it look like? In a cloud chamber, it should give a heavy track of uniform density through its path. This will help distinguish it from such tracks as those of alpha particles, which get denser as the particle slows to a stop. Also, in a strong magnetic field, the new magnetic particle should be deflected toward one of the pole-pieces, instead of running in circles as electrons and protons do.

**Completely Dry Process Developed
For Making Pictures and Printing**

Xerography Dry Photo Process

► A REVOLUTIONARY, completely dry process for taking pictures and printing was revealed recently to the Optical Society of America meeting at Detroit.

Static electricity and dry powders take the place of the familiar chemical solutions used in photography, in the new process called "xerography." Xerography was described by Dr. R. M. Schaffert, head of graphic arts research at the Battelle Institute, Columbus, O., and Joseph C. Wilson, president of the Haloid Company, Rochester, N. Y.

They explained that the fast, new, dry process promises to find uses in both the present fields of photography and printing.

A finished picture can be produced in less than a minute with xerography, they reported. The process is simple enough to be followed by an unskilled person, and prints can be made on a variety of materials, such as glass, cloth, metal or wood, in addition to ordinary papers. Because powder is used, it is possible to make the equipment simpler and less costly than in other methods.

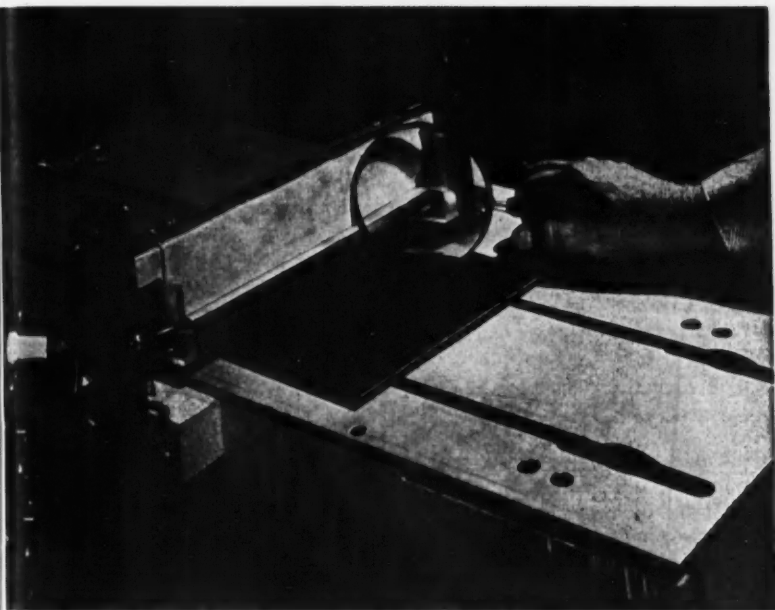
A photoconductive plate, made by coating a back material such as a metal sheet with a photoconductive insulating material, is electrically charged by rubbing it with a cloth or some other method in the dark. This is done immediately before use and makes the plate sensitive to light.

This plate is then exposed to light in a camera, the way that film is used to take pictures. The coating discharges the electrostatic surface charge into the backing wherever the light falls on it. This leaves a latent image on the surface of the plate. Developing is done by flowing a powder over the surface of the plate. This powder includes a superfine developing resin and a coarse carrier material. A mirror-reversed image, like a film negative, results. Printing is accomplished by charging the paper on which the picture is to be printed. The powder is attracted to the charged paper to form the image. Fixing is done by heating the paper print for a second or two.

Black developing powder on white paper will create a black and white print, but other colors may be made for multi-color printing, using separate plate images for each color.

Xeroprinting was described as a simpler variation of the xerographic process. It uses a xeroprinting plate on a rotating cylinder. The plate includes a charging device, a mechanism by which the image is developed with a powder developer, a mechanism for transferring the powder image to paper, a method for fixing the powder to the paper, and cleaning or auxiliary devices as required.

The image plate is evenly charged by a corona discharge device, and the charge immediately passes off the con-



► **ELECTRON SPRAYER**—*This machine, the only specialized apparatus required for xerographic reproduction, is used both to sensitize the plate and to transfer the powder image from the plate to paper by "spraying" electrons from the fine wire visible through the enlarging glass.*

ductive, non-printing surface, while remaining on the printing surface. As the cylinder turns, the plate enters a developing chamber where powder is applied, and on to where the paper and plate are passed under corona discharge points. Here, the image is transferred to the paper, which passes through a heating unit to fix the image.

Xerography was invented by Chester F. Carlson, a New York patent attorney, who patented the

process. He licensed the Battelle Institute to develop it. Mr. Wilson reported that his company is preparing to market a xerocopying machine for reproducing copies of documents of various sorts. Continuing research on the process is also being sponsored by the Signal Corps, Department of the Army. A full scientific report of the work by Dr. Schaffert and C. D. Oughton of the Battelle Institute will be published later this year.

For the Home Lab

Fireworks!

by BURTON L. HAWK

► PUT AWAY the text-book. Temporarily forget symbols, formulae and equations. This month we experiment solely for pleasure and entertainment. And who does not enjoy the colorful sparkling display of fireworks!

General Information

Of course, all fireworks should be set off outside unless you use very small quantities and do not object to irritating smoke. Best results are obtained on dark, wind still evenings.

All ingredients used must be dry and finely powdered. Powdering should be done in a mortar—*each ingredient separately!* Special caution must be observed when grinding potassium chlorate, as this substance may explode if handled too roughly. The powders are mixed together on a sheet of paper by lightly shuffling with a knife or spatula.

The mixed powders are ignited easily by using touch paper. The latter is made by soaking sheets of filter paper in concentrated potassium nitrate solution. When dry, they are cut into thin strips.

Remember the composition of all the following mixtures is given by parts—not by weights. We suggest that you refrain from using too large quantities.

And finally, the mixtures must be made immediately before using for best results.

Colored Fires

Thoroughly mix the ingredients and pour into a metal pan—a metal screw cap jar lid will be satisfactory. Form a neat pile and ignite with touch paper.

White

- 6 parts—potassium nitrate
- 1 part—sulfur
- 1 part—antimony sulfide

Red

- 5 parts—strontium nitrate
- 1 part—sulfur
- 1 part—charcoal
- 2 parts—potassium chlorate

Yellow

- 3 parts—sodium chloride
- 4 parts—potassium nitrate
- 1 part—sulfur
- 2 parts—charcoal

Green

- 7 parts—barium nitrate
- 2 parts—sulfur
- 3 parts—potassium chlorate

Purple

- 1 part—copper sulfate
- 1 part—sulfur
- 1 part—potassium chlorate

Serpent's Eggs

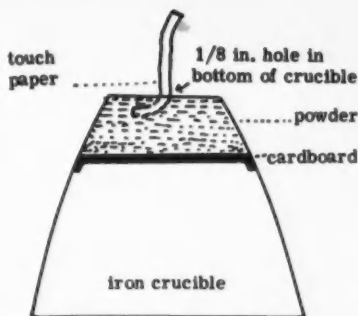
Thoroughly mix together 3 parts potassium nitrate, 5 parts sugar, and 5 parts potassium bichromate. Form a paste with alcohol and mold into pellets. When dry, ignite with touch paper. A bulky snake-like ash is formed.

Flower Pot

Mix together 1 part each of powdered magnesium, powdered iron, charcoal, and sulfur; $\frac{1}{2}$ part of powdered zinc, and 2 parts of potassium nitrate. Now obtain a small iron crucible and drill a small hole in the bottom of it. Insert a strip of touch paper through the hole, extending about $\frac{1}{2}$ inch into the crucible. This will serve as a fuse. Holding your finger over the hole, pour in the mixed powders, until the crucible is about $\frac{1}{4}$ full. Then wedge the mixture in with a piece of cardboard and invert the crucible (see diagram). Ignite the touch paper, step back and witness a brilliant display. The flower pot must be ignited outside, as the flying sparks will attain considerable height.

Sparklers

A mixture of 20 parts potassium nitrate, 6 parts sulfur and one part charcoal is blended together with gum arabic solution to form a thick paste. Obtain several lengths of thin wire strips and dip them into the paste. When dry, ignite with a match.



Flower Pot - cross sectional view

All-Star Sparkling Fire

This fire contains everything but the kitchen sink—which, unfortunately won't burn. Mix together 1 part each of powdered magnesium, powdered iron, charcoal, sulfur, powdered zinc, antimony sulfide, lycopodium powder, cloves, ginger, cinnamon, sugar, and 3 parts potassium nitrate. Ignite outside with touch paper and whee - - - - - aah!

★ ★ ★

Well, the show is over. We hope you have enjoyed it.

Unbalanced Equations

It's a Good Trick If You Can Do It

► "THE MODERN college graduate is a man without morals riding across the earth in a cap and gown with an electronic computer in one hand and a cyclotron in the other."

—John F. McCaw of Indianapolis, as quoted by A.P.

Three Nobel Prize Winners



Three European scientists are the recipients of this year's distribution of prizes in medicine, physics and chemistry among the Nobel awards.

Medicine

► AWARD of the Nobel Prize in medicine to Prof. Paul Mueller of Basel for his discovery of the insecticidal value of DDT re-emphasizes what scientists all know but some of the rest of us may at times forget: the fact that science knows no national boundaries.

Prof. Mueller is a Swiss, and the Geigy Company for which he works is a Swiss firm. But DDT was first made by a German, Othmar Zeidler, in 1874. The prize money comes from the fortune left by a Swede, Alfred Nobel, who first made dynamite by mixing into an inert carrier the too-sensitive liquid high explosive, nitroglycerin, which was the discovery of an Italian, Ascanio Sobrero.

America figures in the story twice. The invasion of Europe by an American insect pest, the potato beetle, was one of the prime stimuli that set Prof. Mueller to searching for a more effective insecticide. Discovery of the value



Paul Mueller

► *For the insecticide, DDT.*

of DDT for this purpose, especially its effectiveness against body lice, came just in time to enable American Army sanitarians to suppress a typhus outbreak in Naples that might otherwise have become one of the worst horrors of the world's most horrible war.

The boundary-crossing benefits of DDT continue and increase. Its use to prevent disease-carrying insects from stealing intercontinental rides on aircraft and ships is now accepted routine. It also aids mightily the efforts of entomologists to prevent the spread of insect pests of cultivated plants and domestic animals. If it could only be used to delouse political heads of their crawling fears, suspicions and hatreds, the peace dream of Alfred Nobel might be measurably closer to realization.



P. M. S. Blackett

➤ *FOR cosmic radiation.*

Physics

➤ "FOR THE DISCOVERY of a connection between magnetism and gravitation."

That might well be the citation of the 1948 Nobel Prize for physics awarded to Prof. P. M. S. Blackett, of Manchester University, one of Britain's outstanding physicists. Actually the award is reported to be "for discoveries in the field of cosmic radiation."

Last year Prof. Blackett presented to the Royal Society of London a mathematical relationship between electromagnetism and gravitation that arises out of the rotation of such massive bodies as the sun, earth and stars.

This formulation was hailed as possibly as significant as the Einstein relationship between mass and energy

(Please turn to page 27)



Arne Tiselius

➤ *FOR electrophoresis.*

Chemistry

➤ FOR NEW METHODS of separating, detecting and analyzing colloids, particularly the large molecules of proteins and other substances so important to living things, the 1948 Nobel prize for chemistry was awarded to Prof. Arne Tiselius, of the Institute of Physical Chemistry, Upsala University, Sweden.

Working in the tradition of Prof. The Svedberg of the same university, who won the same prize in 1926, this year's Nobelist has developed two methods of analysis that are finding increasing use in investigational laboratories.

He applied electrophoresis to the separation of the heavy molecules of protein and other substances. He also worked out a new method of analysis

based on adsorption and applied it to organic and biochemical problems.

The electrophoresis apparatus of Prof. Tiselius acts like a sorting machine for the separation of heavy molecules in solution. Prof. Svedberg is famous for his work on separating molecules and other substances of different weights by whirling them in the centrifuge. But sometimes the centrifuge method of separation can not be used.

Prof. Tiselius made an apparatus that takes advantage of the different electrical changes which protein particles possess to effect the separation. By placing a solution of such particles between electrodes and applying an electrical voltage, it is possible to obtain a migration of the particles. Those with the greater charge move the faster.

The trick of the Tiselius apparatus is to produce a current in the solution flowing against the motion of the particles. Usually the current flows just as fast, in one direction, as the slower of the migrating particles is moving in the other. These particles, therefore, are like a man on a treadmill who, though he walks swiftly, never really does anything but stay in one place.

Meanwhile the particles with the greater electrical charge are moving just a bit faster than the opposing current so that eventually they reach one end of the chamber and the separation has been effected. The Tiselius method has been used in several laboratories in the United States, particularly in connection with study of living tissues.

The method of adsorption analysis cited in the Nobel award makes it possible to separate and differentiate

between proteins, acids, sugars, salts and other substances that are of biological importance.

Adsorption is action of a substance holding another substance on its surface. It is adsorption, not absorption, which is what a sponge or piece of blotting paper does to water.

In past years various kinds of adsorption methods have been used in organic chemistry and biochemistry. Willstätter and his followers used adsorption for the differentiation of various enzymes. Chromatographic analysis which is being applied widely is based on adsorption phenomena.

Prof. Tiselius may be said to have mechanized and made automatic the method of adsorption analysis.

Previous investigators had shown that the chromatography of colorless substances was possible in some cases by observations of the various layers in the column of material upon which the substances being investigated had collected. When the various substances gave a color, their detection was relatively simple. When they were colorless, it was sometimes possible to differentiate them by their fluorescence. Or the parts of the column could be tested with different specific reagents, either on the column directly or after it had been cut into sections and extracted.

Prof. Tiselius worked out a new and more general method. After passing through the column of adsorbent and before any mixing has taken place, the solution is allowed to flow through an arrangement for determining the concentration by measuring continuously some property of one of the chief substances passing through. This is done by connecting the outlet of

the column to a small cell in which the refractive index, light absorption, conductivity or some other suitable property of the solution is observed continuously. The readings are plotted against the volume of flow. Apparatus that is self-registering and operates relatively automatically has been developed.

Physics

(Continued from page 25)

which was given such powerful reality by the atomic bomb. Like $E = mc^2$ the Blackett formula has a cryptic appearance. In it there are: P , the strength of the magnetic field; β , a constant near unity; G , the gravitational constant; c , the speed of light; and U , the angular momentum or spin of a revolving body. The formula is:

$$P = \beta \frac{G^{\frac{1}{2}}}{2c} U$$

In some laboratory at the present time an experimental test of this relationship may be underway, since Prof. Blackett proposed an experimental test. It would consist of revolving a large sphere quite rapidly and measuring its magnetic field.

Whether or not the Blackett formulation proves to be the basic connection between magnetism and gravitation, the earlier researches recognized by the Nobel award made important contributions to the understanding of

the constitution of matter and radiation.

Prof. Blackett was one of the famous Cavendish Laboratory team of physicists that was led by the famous Rutherford. At Cambridge, Blackett studied cosmic rays and found positive electrons (positrons) as well as ordinary electrons bursting out of cosmic ray showers. He was in the group that made positrons artificially. He estimated that the short-lived positrons were so plentiful that they must account for a thousandth part of the whole material universe. This was as early as 1933.

During the second world war, Prof. Blackett gave up tracking cosmic rays and atomic particles to work on Britain's early radar defense system and track Nazi planes instead. But he is back at his research now, famous and fifty, puzzling out more deep secrets of the universe.

Not all his time is spent on research, however. He is an "atom scientist," adviser to the British government on atomic energy. His book titled "Military and Political Consequences of Atomic Energy," published in mid-October, says that Russia would be foolish to accept the proposals of the United States for the control of atomic energy. In his view, the dropping of the atomic bombs on Japan was actually the first act of the cold diplomatic war with Russia now in progress.

Chlorine dioxide, first used to bleach flour less than two decades ago, is now used to bleach starch, paper, soap and textiles.

By agreement between the two countries the United States will buy all pyrethrum flowers grown in Brazil not needed for domestic insecticides.

**Improvements in Steel and Oil
Lead This Month's Patent List**

Patents in Chemical Fields

To obtain complete specifications of any patent, order by number from U.S. Commissioner of Patents, Washington 25, D.C., enclosing 25 cents in coin, money order or Patent Office coupon (no stamps) for each patent.

High-Temperature Steel

► **HIGH-TEMPERATURE** stainless steel, suitable for use in gas turbine engine blades, nozzles, and exhaust valves for internal combustion engines, marks an advance in the development of modern engines that operate at extreme temperatures.

The award, patent 2,447,897, was made to William Charles Clarke, Jr., Dundalk, Md., assignor to Armco Steel Corporation, Middletown, Ohio. The process includes a simple, practical and reliable method for conditioning stainless steels which increases resistance to high-temperature stress-rupture and creep, and makes it tough, strong and durable under conditions of high temperature uses.

This stainless steel, in addition to iron, contains carbon, chromium, nickel, manganese, molybdenum, copper, titanium and columbium. The heat-treatment to perfect the product includes heating up to 2,250 degrees Fahrenheit, at which point all the titanium and part of the columbium go into solution. Then the steel is drenched in air, oil or water, and subjected to a re-heat.

Open Hearth Improvement

► **FASTER PRODUCTION** of open-hearth steel by making initial temperatures much higher is the promise of a new process on which U.S. patent 2,446,511 has been granted to two Canadian metallurgists, F. G. Kerry of Montreal and E. T. W. Bailey of Hamilton, Ont.

Time required for melting the charge of scrap in the furnace is shortened by blowing in a gas containing 60 per cent oxygen—three times the oxygen concentration in the air conventionally used—and increasing the gas or atomized oil fuel by at least 15 per cent. After the charge has been melted, a lower-oxygen blast will suffice, and ordinary air is substituted for the initial enriched atmosphere.

Electroplating Aluminum

► **TWO RICE INSTITUTE** graduates in chemistry participate in three patents on a new process for electroplating aluminum on iron, copper and other heavy metals. They are Dr. F. H. Hurley, now on the Reed College faculty, and Dr. T. P. Wier, Jr., now with the Shell Oil Company at Houston, Texas. The electrolytic mixture is composed of aluminum chloride and ethyl pyridinium chloride. The plating is done in an aluminum pot, which serves also as the anode. All three patents, Nos. 2,446,331, 2,446,349 and 2,446,350, are assigned to the Rice Institute.

Oil Field Aids

► **INCREASING** demands for gasoline, fuel oils and lubricants are reflected in

many new devices for assistance in oil fields. Among new patents are two worthy of mention. One is a method of determining the permeability of the underground layers that form the crust of the earth; the other is a method of electrically logging well bores.

The patent numbers are 2,446,588 and 2,446,527 respectively. The patent for the determination of the nature of substrata was awarded to Gerhard Herzog and Alexander Wolf, Houston, Texas, who have assigned their rights to the Texas Company. Patent for the well-logging method was granted to Melvin E. Chun, Huntington Park, and John C. Stick, Jr., South Pasadena, Calif. It has been assigned to Lane-Wells Company of Los Angeles.

In determining the permeability of the formation surrounding a bore hole by this new method, a radioactive liquid is used. The formation to be examined is filled with this fluid, and a radiation detecting device is lowered within the bore to the impregnated section. Pressure is then applied to the liquid.

In the logging of well bores to determine the type of the surrounding materials what is known as phase shift logging is employed. That is, it utilizes the inductive and capacitive effect of formation traversed by a well hole. In the method, an alternating current field is established in the formation and a probe circuit obtains electrical samples of the alternating current field.

For Rocket Exhausts

➤ **EXHAUST NOZZLE** for rockets and rocket motors, with an asphalt composition protective coating to keep the metal from melting in the extreme

heat of the discharge gases, has received a government patent.

Patent 2,447,200 was granted to Fred S. Miller, Pasadena, Calif., for this invention. His rights have been assigned to the Aero-jet Engineering Corporation of Azusa, Calif. The device has direct application where rocket power is used in aviation. Rocket escape gases may have a temperature of 3,000 degrees Centigrade, which melts many metals.

The asphalt composition employed is a thermoplastic which is used to coat the shoulders and walls of the conical passage leading to the nozzle throat. In action it reduces the heat flow of the escaping gases to the walls of the nozzle. It is chemically inert in the presence of the heated gases, but vaporizes, absorbing heat in the process, thus reducing the effective rate of heat transfer to the nozzle.

This protective coating may be used with both solid and other propellants. In a propellant charge of asphalt as fuel and potassium perchlorate as oxidizer, an excess of asphalt should be used so that the perchlorate is consumed in the combustion chamber and none left to attack the nozzle coating.

Magnetic Method For Oil

➤ A **MAGNETOMETER** which can be used in petroleum explorations, as well as in locating hidden magnetic ores, earned Charles H. Fay, Houston, Texas, patent 2,447,849, assigned to the Shell Development Company of San Francisco. It is somewhat similar to the magnetometers already used in locating underground geological formations suitable for oil deposits, iron ore deposits and, as the airborne wartime doodlebug, for locating submerged U-boats.

The instrument measures magnetic fields, and in so doing gives information helpful in determining geological formation. It comprises a coil pivoted to swing in the magnetic field, a light source, a photo-electric cell, optical means carried by the coil for varying the illumination of the cell with the swing of the coil, and amplifier means to increase the cell's output.

Coal Distillation

► A CONTINUOUS process for a low-temperature method for distilling coal to obtain oil and gas earned Henri Lantz, Paris, France, patent 2,448,223. In addition to coal, the method can be used with lignite, bituminous shales and mineral and organic materials. The patent has been assigned to Societe Chimique de la Grande Paroisse, also of Paris. The distilling retort is a vertical chamber into which the material to be distilled is fed at the top. The process is largely a heating and reheating procedure.

An attachment to the exhaust outlet of gasoline and other internal combustion engines, particularly for places where the atmosphere may contain explosive amounts of gases, is a device for separating dangerous sparks and hot carbon particles from the exhaust fumes. It also decreases exhaust noise. Harvey Ellis Davidson, Tulsa, Okla., received patent 2,448,420 for this invention.

Chemical Separations

► AMONG the many chemical patents issued is an improved process for the manufacture of sodium percarbonate, the separation of chlorides from potassium carbonate, and the extraction of the medical drug rutin from such vegetation as fresh buckwheat plants.

Two citizens of England received

patent 2,448,058 for the sodium percarbonate process, Victor Wallace Slater, Luton, and William Stanley Wood, Harpenden. Robert D. Pike, Pittsburgh, received patent 2,448,191 for the second process. Roderick Koenig Eskew, Glenside, Pa., received patent 2,448,175 for the rutin extraction method and has assigned it to the U.S. Department of Agriculture.

Hydrocarbon Peroxides

► CHEMICAL patents of interest include improvements in the method of production of hydrocarbon peroxides, additives for silicone oils to improve lubrication, and a simple method of treating water for removing scale-forming ingredients and other impurities, and particularly for removing silica.

Patent 2,447,794 was granted to Philip D. Brewer, Long Beach, Calif., for the first. It has been assigned to Union Oil Company, Los Angeles. Patent 2,447,483 was awarded to Hayward R. Baker, Mount Rainier, Md., and William A. Zisman, Washington, D.C., for the second. It has been assigned to the Secretary of the Navy. The water-treatment method earned Walter B. Leaf of Denver, Colo., patent 2,447,511.

The object of the first invention is to provide a method for the controlled liquid phase oxidation of hydrocarbons to produce more hydrocarbon peroxides. Silicone oils, by themselves, are somewhat corrosive. The additives used in the new mixture are organic compounds which are soluble and compatible with the silicone oils at high and low temperatures, and they inhibit the corrosive action of the oils when dissolved in them in small quantities.

The Atomic Nucleus

A New World to Conquer

by DR. I. I. RABI
Columbia University

Address delivered at the dedication of the Laboratory of Nuclear Studies at Cornell University.

► THE ELECTRICAL constitution of matter, that is, the fact that matter is made of constituents which are electrically charged positive and negative, was clearly understood only at the turn of the last century. The fundamental fact of atomic structure, that the atom was made up of a central positive core, the nucleus of the atom, which was positively charged and surrounded by electrons charged negatively, was realized only after 1911 from the great work of Rutherford.

However, it was not until after the work of Bohr, Einstein, Schrodinger, Hisenberg, Pauli, and Dirac, that we had adequate intellectual tools to understand atomic structure. By the end of 1928 the job was complete. The fundamentals had been understood and the structure of the atom was a problem which, in principle, had been solved. The atom had been conquered, but conquest and consolidation are two very different things.

Newton almost three hundred years ago gave the fundamental theory of the solar system and celestial mechanics, yet there are astronomers and mathematicians working on these very problems even today. One hundred years from now there will be physicists, chemists, and engineers working on important problems of atomic and molecular structure.

Long before the fundamental principles of atomic structure had been understood, very important advances had been made both in theory and application because practical results do not depend on detailed knowledge of the basic laws.

Our subject today, however, is not the structure of the atom but the atomic nucleus. However, in assessing our present position on this problem and forecasting the future there is much we can learn from the development of our attempts to understand the atom. Let me sketch very briefly the fundamentals of the problem.

If an atom of uranium were magnified a billion times, it would be the size of a basketball, and if its weight were increased correspondingly, it would weigh about a ton. If one were to examine it carefully, one would at first sight see nothing at all, but on very close inspection one would find 92 tiny particles, each much smaller than the point of a very fine needle, moving with enormous speed, approximately inside the confines of the basketball. These are the electrons. Altogether these electrons, small as they would appear, would weigh one half pound.

In the center one would discover a speck of dust about 1/1,000 of an inch in diameter. This is the nucleus of the atom. Its weight or mass would be a ton, less a half pound, of course, for all the electrons put together. If we take,

with Einstein, the famous relation $E = MC^2$, that is, energy is proportional to mass, we see that almost 99.99% of the energy of matter is locked up in the nucleus.

The useful energy we have had available up to the present from fuels such as oil, coal, or food has been chemical energy and generally less than one billionth of the total conceivable energy which is locked in the atom and more particularly in the nucleus. These numbers stir the imagination. They are inspiring and frightening, especially if we remember Hiroshima.

However, I am not predicting the release of these stupendous powers. We have a long way to go before we can even begin to assess the validity of such speculations. Let us examine further this speck of dust we called the nucleus of the uranium atom.

Looked at more closely it would turn out to be comprised of 238 objects, 92 protons all positively charged and 146 neutrons, 238 in all. I did not pick uranium 235 because that is fissionable material and is classified secret. The protons are all positively charged and have the same charge as the electrons. The neutrons have no charge at all.

We now come to the fundamental question. What forces keep this conglomeration of protons and neutrons together against the mighty repulsions of the protons for one another? What force keeps these nuclear particles which move at tremendous speeds from flying apart in less than one billion billionth of a second? I don't know. Neither does Professor Bethe, even though he knows what makes

the sun shine so brightly; nor does anybody else in the whole world.

There are some charming speculations which may contain some grains of truth. I will tell you something about them, but first I must say that our ignorance is not entire. Although the why of nuclear forces is not known, we have a very definite notion about the magnitude of these forces. Otherwise the atomic bomb could not be made and we could not be seriously discussing the use of nuclear energy for the production of power. Application of scientific discovery does not have to wait on complete understanding of the whys and wherefores.

The utilization of atomic energy, whether for warfare or the greater arts of peace and healing, does not await a great basic discovery. The fundamental science is at hand, and it is a question for the engineer, the chemist, the metallurgist, and applied science in general.

At this dedication of the Institute for Nuclear Physics we are concerned with much more fundamental questions which look beyond the immediate practical problems of today but which may bring the headaches of the future. We will now proceed from what may be considered the more or less well-known to what is known only partially and on into the unknown.

At this point the taxpayer, the proverbial hard-headed businessman, or even the average man about town or Congress may say: Stop! Haven't you made trouble enough? Why not take a recess from your fundamental problems and let us make some order of the mess you have just dropped in our laps? Why not go off and study some

politics, economics, sociology, psychology, or even psychoanalysis, and help us solve our vexing problems of human relations and organization? Sufficient unto the day is the evil thereof.

One can say a number of things in reply. In the first place, we are far too busy to stop. Science just can't be turned on and off. We, in common with the rest of humanity, are embarked on an adventure from which there is no turning back. We always have to learn more in order to get along with what we have. Who knows what great discovery awaits us tomorrow or the next day? One can hint darkly about our competitors both present and prospective.

One could give the easy, truthful answer that the solution of these problems has almost always paid high dividends in the material welfare of the nation. It has increased production, improved transportation and communication. It has helped combat illness and disease. It has been a powerful weapon in the battle against ignorance and superstition.

This is essentially the answer of the alchemist to his patron. Give me a laboratory and equipment, support me in my experiments, and I will find you the philosopher's stone which will make you richer, healthier, and more powerful. He asked nothing for himself but the love and favor of his noble patron. That the ancient alchemists discovered many important and useful things, there is no doubt. They did not find the philosopher's stone. We, their descendants, have come somewhat closer to the goal and much of the alchemist's attitude survives into the present day.

The extreme of this attitude is to

be found in Soviet Russia. There the scientist holds a very high place in society. Although his altitude is high, his permissible horizons are narrow. He is expected to produce discoveries which will not only strengthen the State but which will support the doctrines of the dominant group. For success he receives great rewards, country estates, servants, Lincoln limousines, and well-equipped laboratories. I have heard on good authority that when the atomic bomb exploded over Hiroshima the salaries of Soviet nuclear physicists were trebled. These are mighty great incentives. No prize stallion or highly bred milk cow could have better treatment, but I doubt whether the Soviet scientists find happiness and inspiration in their exalted condition.

From the standpoint of basic science such limited and materialistic motivation is irrelevant and even vulgar. One might as well give a social motivation for artistic creation in that it attracts tourists, or for poetry that it ultimately freshens up the phraseology for advertising slogans.

The real reason for basic research is to expand the boundaries of knowledge pure and simple. It is an expression of the human spirit. This passion for new knowledge, for the exploration of nature is strong in some, easily controllable in others, and in many people completely absent. Various societies have differed in this respect. The Athenians were passionately devoted to the search of abstract knowledge. The Spartans, on the other hand, were quite indifferent.

Fortunately we are living in a time in our country when the interest in scientific research and discovery is

mounting very rapidly. This new Institute for Nuclear Science is one of the many expressions of this interest. The great telescope on Mount Palomar is another. All over the country great new laboratories are arising in all fields. Schools of art and music are multiplying. The country is growing up and some of the energy which went into the conquest of this continent is turning toward intellectual and artistic endeavor. We may see the dawn of a Golden Age. Perhaps it has already come and we are no more aware of it than the Athenians in the time of Pericles.

Let us return to the examination of the atomic nucleus just for the sheer pleasure and interest of it. To study an object as small as the atomic nucleus is even more difficult than it sounds. In the first place, you know that one can see smaller objects with the ultraviolet ray microscope than with an ordinary microscope using visible light. The reason is that the wavelength is shorter in the ultraviolet. More recently you have heard of the electron microscope which sees things even smaller, because electron waves can be utilized which are very much shorter. The large synchrotron which is now nearing completion will produce electron wavelengths and gamma rays which are a sort of super-short ultraviolet, of approximately the size of the nucleus. In a certain broad sense the plan is to take a look-see at the atomic nucleus with these extraordinarily powerful instruments.

What will Professor Wilson and his crew of merry men see? If he knew, he would not have built the instrument, but we can conjecture some of the strange things he might see and

study. In the first place, the energy of the radiation, although compressed in volume, comes in such enormous packets of about 300 million volts, compared with 3 volts of ordinary light, that mostly chips in the form of protons and neutrons will come out of the nucleus. These chips will interest them enormously but will probably not be the main show.

The chief phenomenon will be in the class which has already been observed in cosmic rays and in the large synchrocyclotron at Berkeley. When these ultra high energy particles strike a nucleus, new particles come out which were not supposed to be there in the first place. They cannot be within the nucleus for reasons which would be too lengthy to give in this lecture. Yet they come out of the nucleus under the extreme condition of high energy impact. The only possibility is that they are created then and there on the instant out of the energy of the collision.

This fascinating phenomenon was first observed about 15 years ago by Carl Anderson in Pasadena. When gamma rays of over a million volts energy strike an atomic nucleus, a pair of electrons comes out once in so often, one positive and one negative. Vice versa, a positive electron and a negative electron can combine leaving nothing but gamma radiation, which is pure light energy.

In the big Berkeley cyclotron it was observed only a few months ago by Lattes and Gardner that when a 400 MEV nucleus of helium struck a carbon nucleus, a new particle appeared, perhaps identical with one previously observed in cosmic rays by Powell and his group in Bristol, England, about a

year ago. This new particle has been called a pi meson. It is about 300 times as heavy as an electron and can have either positive or negative charge. The pi meson does not last very long, only about one hundred millionth of a second, and then it turns into two other things. One of these is another kind of meson of about 200 electron mass units. The other partner is at present unknown.

This phenomenon was first observed in cosmic rays by the Bristol group about eighteen months ago, although we have no real assurance that the Berkeley and Bristol phenomena are identical. You see that the Cornell synchrotron is coming into existence in a very exciting time and is bound to play an important role of discovery. The mu meson, which may be identical with a particle which Anderson in Pasadena and Street in Harvard found in cosmic rays about thirteen years ago, does not linger with us very long either. After about a millionth of a second it turns into an electron and something else which is also unknown.

What do these phenomena mean? It is far too early to tell. No one knows how many more particles will be found in the next few years, after the new machines are in operation, or perhaps in the next few months or days.

Yet, strangely enough, some of these discoveries were foreshadowed in 1935 by the Japanese theoretical physicist Yukawa. He was then about 27 years old. He reasoned from the fact that nuclear forces were short range like the cohesive force of a glue which is very strong on close contact but disappears on a small separation, that the forces could not be electrical in na-

ture, since these are long range forces like gravitational forces.

On the other hand, if one postulated that a proton or neutron in a nucleus could spontaneously emit a massive particle which could be absorbed by another proton or neutron, and vice versa, such short range forces could be explained. Shortly afterward, following this same lead, Anderson and Street independently discovered the mu meson which could be such a particle but isn't. Perhaps the pi meson is this Yukawa particle. It has been suggested with justice that they be called Yukons.

We see that somehow there may be a connection between these new particles and nuclear forces. Why there are so many, why they should disintegrate so quickly and spontaneously, we don't know. We don't know how many there are, or just how they behave in the neighborhood of a nucleus, or anything solid about them really. The young men and women here who expect to be physicists will have plenty of problems to study.

Before I close I want to tell you of the most charming new particle of all, the neutrino. This particle has never been observed at all, but, like the God of the philosopher, if it did not exist it would have to be invented. It comes about in this way. Some nuclei, like rubidium or potassium, spontaneously emit electrons and change into another kind of nucleus. Yet there cannot be any electrons within the nucleus itself. They are just created and come out. On the other hand, they do not all come out with the same energy even though there is a definite energy difference between the energy of the original and final nucleus. This is more

than tragedy, because the law of the conservation of energy, without which we would not know how to turn around in physics, says that any energy lost must appear in some other place. That is where the neutrino comes in; it is a particle invented to carry off the missing energy in order to keep the books straight. There is a similar law about spin, and the neutrino takes care of that, too. It is a most convenient little gadget.

After it had been invented, consequences as to its properties could be drawn fairly easily. The most striking property is that it has no mass whatever. It interacts with matter so slight-

ly that it could pass right through the earth in its thickest part without hindrance. For this reason there is no known way of detecting it. It is merely the subject of the verbs "to be" and "to spin."

I hoped in this talk to show you that we physicists don't know everything. That it is not a depressing subject, hopelessly involved in atomic warfare, but a great and exciting, civilized, intellectual adventure. Your new Institute of Nuclear Physics puts you right in the center of this wonderful life, and I wish you joy and great discoveries.

Electric Charge Preserved in Ice

► A METHOD for literally putting an electrical charge on ice and later releasing it was reported at the meeting of the American Chemical Society by Dr. Wendell Latimer, dean of the University of California College of Chemistry.

Dr. Latimer said that if a potential of 1,000 volts of electricity is placed across a cube of ice and the ice is suddenly cooled with liquid air, an electrical charge will be "preserved" in the cube. The 1,000 volts again become available if the cube is warmed up.

The chemist explained that the molecules of many substances are little

dipoles; that is, one end of the molecule is charged positive and the other negative. When an electrical field is applied to such a polar substance, the molecules tend to orientate themselves with the field.

Dr. Latimer said that because of the rigid lattice structure, the molecules of ice have difficulty in rotating. The scientist proposed an unusual mechanism for this reorientation. He said it is accomplished by the hydrogen nuclei, or protons, jumping from one molecule to another over a high potential barrier. At low temperatures the protons lack the energy to enable them to make these jumps.

There is a definite connection between the kind of fertilizer used on the soil and the nutritional value of the products grown in it.

Plastic fifes and bugles make marching music and chow-calls in the Army.

New Tests For Paints

► AN ELECTRICAL testing method that is helping chemists develop completely waterproof paints was described to the American Chemical Society by Dr. Max Kronstein and Marion M. Ward of the New York University College of Engineering.

Paint and varnish coatings usually break down when moisture penetrates and undermines them. The new method reveals flaws and pores as tiny as a pin point.

Paper soaked with a salt solution is sandwiched between a plate of aluminum and another of iron, which has been painted. Then the metal plates are connected to opposite poles of a battery.

If the paint surface is not impervious to water, the salt solution seeps through and with the aid of the electric current floats away tiny specks of iron, depositing them on the wet paper.

The paper is removed and treated with a mixture of two chemicals, potassium ferrocyanide and potassium ferricyanide, that combine with the iron and form a vivid blue color. The process is almost identical with the making of blueprints. The test gives a permanent map showing the size, shape, and location of every flaw.

By making the test before and after the coating has been exposed to salt atmosphere, ultra-violet light, or other destructive elements, it is possible to evaluate the coating.

The method has been used successfully to evaluate coatings before and after certain normal test procedures, such as salt-fog and Weather-Ometer tests, and in quickly comparing the effect which is produced by certain modifications of coating compounds.

Thus a set of electrographic prints, together with a 48-hour salt-fog exposure and a repeated set of prints, gives concrete data for evaluating and comparing paint modifications and treatments. The method has also been used successfully in detecting mechanical damage to a coating and the amount of subsequent spreading of moisture under the coating from the damaged area.

Ultra Sound Tests Paint

► SOUND TOO shrill to be heard by human ears can now tell whether a paint or varnish will wear well. It can do it in less than a second.

This modern test to tell whether a synthetic coating will peel before it should was reported to the American Chemical Society meeting by Saul Moses of the Naval Research Laboratory, Washington.

The coating is smeared on metal which is then shaken violently electronically by a device that generates high frequency sound waves. The force of vibration needed to make the paint or varnish peel indicates how long it can be expected to last under normal conditions of wear.

The new machine makes it possible for the first time to measure the adhesiveness of synthetic organic paints and varnishes accurately and directly.

Efforts to evaluate adhesion date back to the early part of this century. Prior to that time, simple scratch and finger nail tests were used. Methods have been developed to measure forces related to adhesion—all of which are comparative and ac-

tually do not measure adhesion but depend on some related property, such as toughness, brittleness, cohesion, or elasticity.

The caps to which the coatings are applied can be made of any metal and subjected to any aging conditions, thus enabling the tester to find out how well paints and varnishes withstand exposure to weather, corrosive chemicals, and wear.

Seedcorn Damaged by Rays

► ATOM-BOMB rays powerful enough to kill men or animals, released at the first Bikini burst, failed to kill grains of seedcorn exposed on the decks of the target ships, but did cause them to produce plants with many defects and abnormalities. First results of these experiments were described in detail in *Science*, just two years and one day after the burst by Drs. L. F. Randolph, A. E. Longley and Ching Hsiung Li, Cornell University botanists.

Two kinds of seedcorn were used in the tests, one a single-cross hybrid field corn, the other an inbred sweetcorn strain. Twenty-five packages, each containing from 1,500 to 2,500 grains, were exposed on ships in the target array, at varying distances from the center of burst. Similar lots were exposed to graded X-ray doses, from 5,000 to 25,000 Roentgen units. Finally, samples of both kinds of seed were kept untreated, for planting as controls.

As soon as the irradiated seed had been returned from Bikini, portions were planted at the U.S. Department of Agriculture experiment station at

Beltsville, Md. Other plantings were made at the experimental farm of the California Institute of Technology, all three groups of seeds included.

The untreated control seed produced plants of the uniform types expected of corn bred by modern methods. Both the Bikini seed and the X-rayed seed produced many abnormal plants. Some of these had twisted, crinkled, diminutive or otherwise deformed leaves. Other leaves, normal in size and shape, had areas lacking chlorophyll, the green food-making substance, or else completely dead spaces which often resulted in lengthwise splitting.

Tassels also were aberrant, producing as much as 50% of dead or otherwise abnormal pollen. Microscopic examination disclosed derangements and partial destruction of many of the heredity-controlling chromosomes in the cells.

X-rayed seed exposed to doses of between 10,000 and 15,000 Roentgens produced plants most nearly resembling those that came from the Bikini seed, although the similarities did not amount to identity.

Anhydrous Ammonia Fertilizer

► ANHYDROUS AMMONIA is becoming an important fertilizer. Dr. W. B. Andrews of the Mississippi Agricultural Experiment Station has reported to the American Society of Agricultural Engineers that over 200,000 acres of corn and cotton were fertilized by it during the past season.

Anhydrous ammonia is a gas which is compressed to a liquid for handling in commerce, and for application to the soil. It is put some six inches under the soil by means of a knife-type opener or other suitable device, and immediately covered with earth to prevent its loss to the air.

When applied to the soil, ammonia combines with the clay and organic matter to form solids. Its value as a fertilizer is the nitrogen in it. So long as nitrogen in the soil is in the ammonium form, it is not leachable. In fertile, well-aerated soils, ammonia is converted into nitrates within four to six weeks.

Anhydrous ammonia is now being used partly because of the shortage of other sources of nitrogen. Its continued use will depend upon prices and adaptation of machines for its application.

Riboflavin for High Altitudes

► THE BODY cannot adjust to conditions of high altitude without an adequate supply of riboflavin, or vitamin B₂, it is indicated in experiments at the University of California, which also provide further evidence that this vitamin is essential in carbohydrate metabolism.

If the body has a sufficient supply of riboflavin it makes an unusual adjustment to the low pressure of high altitude. The body burns up carbohydrates faster to do the job ordinarily done by a normal supply of oxygen at sea level.

Dr. Agnes Fay Morgan, noted nutritionist and professor of home economics, and Mary Wickson, researcher, found that in riboflavin-deficient rats this adjustment to an increased

consumption of carbohydrates is not made.

However, if injections of riboflavin are given the deficient rats just before exposure to high altitudes, the adjustment is almost normal. The work indicates that persons flying at high altitudes should be given adequate supplies of riboflavin. While the research was done to aid in combat warfare, it is also applicable to peacetime flying.

Dr. Morgan said also that the results may indicate that persons living in mountainous areas at high altitudes may need extra supplies of riboflavin to insure an increased carbohydrate metabolism to compensate for a decreased supply of oxygen in the air.

Fish liver vitamin oils are being made by four factories in the Union of South Africa.

Rubber Freezes Slowly Over
A Wide Range of Temperature

The Strange Behavior of Rubber

by HUBERT M. JAMES
Purdue University

An address before the meeting of the American Association for the Advancement of Science in Washington. The first part concerns general ideas to which many workers have contributed, but the latter part describes a new theory of the structure of frozen rubber.

► COMMERCIAL RUBBER is prepared from a material, *milled rubber*, which is essentially a liquid made up of long flexible rubber molecules. The viscosity of this liquid is very great, because the entangling of the molecules impedes their relative motion, but it will not return to its original shape after it has been deformed.

The fact that rubber molecules form a liquid at ordinary temperatures tells us something about these molecules: the forces between them are not great enough to suppress their relative motions, for this would convert the material into a glass; neither are these molecules easily arranged into regular arrays, to form a crystalline solid. Both these things do happen at lower temperatures, but it is very important that the melting point of rubber is below normal temperatures, for its useful properties depend on its being *essentially a liquid-like mass of long flexible molecules*.

Milled rubber is converted into commercially useful rubber by a process of cure, or vulcanization. This

consists essentially of the formation of a relatively few firm chemical bonds between the long molecules, which are thereby linked into a flexible molecular network that extends through the whole material. This network is very irregular in its structure, because the molecules are linked together essentially at random, and the component segments are twisted and cooled like high polymer molecules in solution. Unlike the original liquid, however, the cured rubber is coherent, not easily pulled apart, because the molecules are linked together by firm chemical bonds.

It must be emphasized that, even after this network is formed, the local structure of the material is still that of a liquid. Only a relatively few of the isoprene groups in each molecule—of the order of 1 in 100—are involved in bond formation during cure, and only these small parts of adjacent molecules are brought into fixed relations to each other. For the most part, the structure of the material remains that of a liquid, and the molecules move past each other, in the Brownian motion, about as freely as before. This freedom of motion has been proved in a very direct way by observation of nuclear relaxation times, which depend mainly on the relative motions of adjacent atoms: in rubber these have the low values characteristic of liquids, rather than the high values observed in glasses

and crystals. Since rubber has the structure of an organic liquid, its bulk properties, such as compressibility and thermal capacity, are comparable to those of other organic liquids.

The useful properties of rubber do not depend on its special chemical composition, but only on its being a strong and flexible network of molecular chains with a freezing point below ordinary temperatures. Knowing this, the rubber chemist knows in a general way how to proceed in producing a new rubberlike material. He must start with, or arrange for the production of, long flexible molecules. He must choose molecules which do not exert too large forces on each other, avoiding the presence of too many polar groups; otherwise he will get a glassy or hard plastic. He must make sure that the chains are not too easily packed together into crystals, by having side chains present, or making the main chain itself irregular in structure; otherwise he will get a rigid and probably brittle solid. And, finally, he must arrange for the linking together of these molecules at enough, but not too many points: otherwise he will get a liquidlike milled rubber, or a brittle substance like ebonite.

With this picture of the structure of rubber, one can understand a great many features of its behavior. First let us consider its behavior under stress.

One of the most striking properties of rubber is the ease with which it can be distorted. To stretch equally a wire and a rubber band of the same size, one must apply to the wire a

force that is a hundred thousand times greater. It requires a large force to stretch the wire because in doing so one must change the distances between its atoms, which are all firmly bound together in crystalline arrays. In rubber, however, this is not the case: when rubber is stretched the coiled flexible segments of the network are partially straightened out, but their actual length, and the separation of adjacent atoms in them, need not be increased at all. For the rest, the molecules in the rubber move past each other much like the molecules in a liquid undergoing deformation. Only when the rubber network is stretched to essentially its full length does one begin to pull against firm chemical bonds and encounter strong resistance to further stretching.

Retractive Forces

In view of the liquidlike structure of rubber, the problem is not to explain why the retractive forces in rubber are so small, but why there are any retractive forces at all. If rubber is so much like a liquid, why does it tend to retain a definite form? The key to this problem is provided by some other peculiarities in the behavior of rubber.

When a wire stretched to a fixed length is heated, it expands; the tension in it decreases and even disappears, and the wire sags. A stretched rubber band behaves quite differently: when it is heated the tension in it increases almost proportionally to the absolute temperature, just as does the pressure in a gas heated at constant volume. Now, as you know, a gas exerts a force on the walls of a vessel containing it because its mole-

cules are in constant motion: the pressure is the average force due to impacts of molecules striking and rebounding from the walls. An increase in the temperature involves an increase in the speed of these molecules; they strike the walls more often and more violently, and the pressure is correspondingly increased. Stretched rubber behaves similarly because the forces it exerts are also due to the thermal motion of its component molecules. To understand this it will be sufficient to consider a single flexible molecule with its ends held in fixed positions by external constraints. The molecular chain, in its thermal motion, will jerk against these constraints. When the ends are held together, the chain jerks on each end with equal probability in all directions, and the *average* force on the ends is zero. The more widely the ends are separated, the greater will be the probability that each end will be jerked toward the other, rather than away from it. Thus the jerking of the chain produces an average force tending to pull the two ends together—a force which is greater the greater their separation, and the higher the temperature. In the same way, the retractive force, or tension, in a stretched rubber band is due to the jerking of the thermally agitated molecules which make it up.

This picture of the origin of the retractive forces is correct and useful, but it does not provide a convenient basis for quantitative calculations; for this it is necessary to approach the problem in a different way. Let us now consider a *free* and perfectly flexible molecule sub-

ject to thermal agitation. There is nothing in this situation to make any configuration of the molecule preferable to any other; this molecule will then, in the long run, spend equal times in all possible configurations. Now the possible coiled and twisted configurations of a molecule enormously outnumber the relatively straight ones. Consequently, if we examine such a molecule at any given time the probability is overwhelming that we will find it in one of the coiled configurations, with its ends close together. Indeed, if we were to straighten it out forcibly, a little later we would again find it with its ends close together, in a coiled and twisted configuration assumed through the Brownian motion of its thermal agitation. Thermal agitation, then, tends to bring the ends of a flexible molecule close together, just because a small separation of the ends is consistent with so many more configurations of the molecule than is a large separation. In the same way, a piece of stretched rubber will return to its original form, because it is that form which is consistent with the greatest possible number of configurations of the molecular network. . . .

Ideal Rubber

An ideal rubber may be defined as a liquidlike mass of flexible molecules linked into a coherent network, and having the following idealized properties:

(1) The segments of the network are all very long as compared with the mean distance between their ends. As a consequence of this assumption, one can treat all segments in the same way, regardless of their detailed struc-

ture. This assumption, then, corresponds to treating the molecules of an ideal gas as mass points.

(2) The energy of interaction of the molecules is constant. This corresponds to a similar assumption in ideal gas theory.

(3) The volume-filling property of the chains can be neglected, except as this determines the constant volume of the material. This assumption is, on the face of it, quite unrealistic, and it requires an elaborate argument to show that it need not affect the calculation of retractive forces. . . .

Like a Gas

Real, nonideal rubbers deviate from the ideal in the same way, and for essentially the same reasons, as non-ideal gases. There is a deviation at high extensions due to the finite length of molecular segments, just as there is a deviation in gases at high compressions, due to the finite size of gas molecules. There are deviations in both systems due to the energy of interaction of the molecules. And, finally, in both systems there are very large deviations from the ideal whenever a phase change begins to take place. In the case of rubber this phase change is crystallization, and it is largely responsible for the rapid increase of stress in rubber at large strain.

Previous attempts to explain the effect of the crystallization of rubber on its elastic modulus have been based on the idea that the freezing of rubber is an equilibrium process, like the ordinary freezing of a liquid. These theories lead always to conclusions which are in complete contradiction with observation: they predict that the tension in stretched rubber will be

lowered by its crystallization, whereas in fact it is raised.

Actually the freezing of rubber is not at all an equilibrium process, and—as was first suggested by Flory—the deviation from equilibrium can not be neglected in analyzing the behavior of stretched rubber. A complete analysis of its effect has not yet been made. In preparation for this I have, however, developed a theory of the freezing of rubber which seems to give, for the first time, a consistent explanation of the many peculiarities in its behavior.

Freezing Behavior

The normal behavior of substances on freezing is that of water, which freezes at a quite definite temperature (0°C) as heat is removed, and melts at the same temperature when heat is added. The behavior of rubber is much more complex. It does not have a definite freezing point, but freezes rather slowly at any temperature between -50° and $+15^{\circ}\text{C}$. It freezes most rapidly when its temperature is -25° , and about a tenth as fast when its temperature is as high as -5° , or as low as -45° . Neither does it have a definite melting point: it melts at a temperature that depends on the temperature at which it was frozen, and on the length of time during which it remained frozen. The three essential features are these:

1. Since the melting point of freshly frozen rubber always lies above its freezing temperature, the liquid and solid phase are never in equilibrium.

2. The lower the freezing temperature, the lower is the melting point range.

3. The lower the freezing tempera-

ture, the broader is the melting point range.

To show how peculiar this behavior is, let us suppose that rubber frozen at -30° is placed in ice water. As its temperature rises it will proceed to melt, and the melting will be complete as it reaches the temperature of the water. But then it will immediately begin to freeze all over again, even though the temperature is quite constant, and will thereafter melt only at a still higher temperature.

It must be emphasized that this applies only to freshly frozen rubber, for the melting point of rubber becomes higher the longer it is kept frozen. For instance, rubber kept frozen for some years has been found to melt as high as 43°C , a temperature uncomfortably hot to the hand.

Now, the easy way to freeze rubber is not to cool it at all, but to stretch it. The stretched part of the rubber I hold in my hand is already more completely frozen than if it has been in ice water for many hours, though it is some degrees above room temperature. When I release it, it remains frozen for a moment, but I can feel it contract as it thaws out from the heat of my hand. This simple experiment illustrates the speed with which stretched rubber freezes, and its high melting point. Indeed, strongly stretched rubber will remain frozen well above the boiling point of water.

We have seen that rubber frozen by cooling has a melting point which depends on the freezing temperature. In the same way, the melting behavior of rubber frozen by stretching depends on the degree to which it was

stretched. Rubber frozen by a relatively small extension melts very slowly, whereas rubber frozen by a larger extension melts rapidly and at a lower temperature.

All these features in the behavior of rubber, and many more, can be understood in the following way.

Supercooling

First of all, it must be borne in mind that *supercooling* plays a very important role in the behavior of rubber. Supercooling occurs also in ordinary liquids; water, for instance, will remain in the liquid state 20°C below its normal freezing point if it is kept perfectly free from dust. This happens because the freezing of water, or any liquid, proceeds in two steps:

- (1) The formation of very tiny crystals, or crystal nuclei, containing, say, 10 or 20 molecules, and
- (2) The building up of these nuclei as water molecules adhere to their surfaces.

The normal freezing point of a liquid is the temperature at which the second of these processes can proceed freely; formation of the tiny crystal nuclei is not usually necessary, since dust particles in the liquid play the same role. If the liquid is dust free, however, freezing can proceed only after crystal nuclei are formed. We must now examine this process.

At the freezing point, there is equilibrium between a liquid and a large crystal of the material; molecules pass with equal probability from the liquid to the solid, and from the solid to the liquid. Now the molecules in a very tiny crystal are less firmly bound together than the atoms of a large crystal, since each molecule has, on

the average, fewer neighbors to attract it. A small crystal will therefore lose molecules more rapidly than it gains them, and thus melt, at a temperature at which a large crystal will be perfectly stable, or even tend to grow in size. In other words, the melting point of a crystal is lower the smaller it is. At any given temperature below the normal melting point there will be a critical crystal size, such that larger crystals will tend to grow in the liquid, and smaller ones to melt. Freezing will then proceed only when there appears in the liquid a crystal above this critical size.

How Crystals Grow

If no such crystal nuclei are originally present, how can they come into being, when all smaller crystals tend to melt, rather than to grow? The answer is: by chance. As the molecules move about in the liquid some of them will from time to time form little crystalline arrays. The vast majority of these will be below the critical size, and will break up immediately, but after a time one above the critical size will be formed, will begin to grow in a stable way, and will lead to freezing of the liquid, even though no other nucleus appears. If the temperature is too close to the normal freezing point, the critical size will be very large, and one will have to wait a very long time for a nucleus to appear; if, on the other hand, the temperature is made low enough the critical size will be small, and only a little time will elapse before one or more nuclei appear and the liquid freezes.

The freezing of rubber proceeds in

the same way, except for one complication. Because the molecular chains in rubber are linked into an irregular network, the growth of a rubber crystal about any single nucleus is sharply limited. X-ray studies by Hengstenberg and Mark indicate that the length of the little crystals in rubber is of the order of some hundreds of Angstroms—that is, about the length of segments in the molecular network—and the other dimensions are considerably less. Thus no single crystal nucleus can lead to the solidification of the entire mass of rubber; instead, the rate of freezing of the rubber is determined by the rate at which crystal nuclei are formed throughout the material. As the temperature is lowered below 15°C the critical size of the nuclei is decreased, and their rate of formation is correspondingly increased. If the temperature becomes too low, however, motion of the molecules is greatly impeded, and the rate of formation of nuclei decreases, even though they need not be so large as at higher temperatures. Below -50°C the rubber becomes a glassy solid.

The importance of nuclei in the freezing of rubber is evident from the fact that frozen and then imperfectly thawed rubber refreezes much more quickly than rubber that has never been frozen—evidently because of the presence of crystal nuclei left over from the previous freezing.

These ideas also form a basis for understanding the rapid freezing of stretched rubber. Stretching of rubber forcibly aligns the molecular segments to a considerable degree, though of course less completely than if they

were in a crystal. This reduction of the difference in structure of the liquid and frozen material has the following effects:

(1) it reduces the tendency of molecular chains to leave the crystals, and thus raises their melting point;

(2) for the same reason, it reduces the critical size of crystal nuclei; and

(3) it reduces the rearrangement of molecular chains required in forming a crystal nucleus, thus increasing the frequency with which they are formed.

The latter two factors are, of course, those which cause the freezing to be so rapid.

We have now to consider why it is that frozen rubber has properties which depend on the temperature—or extension—at which it becomes frozen. It is in this respect that frozen rubber differs completely from frozen water. This difference is due to the fact that all water molecules are equivalent in the formation of a crystal, whereas each molecular segment in rubber is permanently distinguished from all others by its special position in the molecular network.

Let us consider a crystal surrounded by molecular chains in the liquid state. These chains will be subject to varying degrees of average tension, depending on their position in the network, and will be moving about mean positions at various distances from the growing crystal surface. Now molecular segments which, on the average, lie parallel to the fiber axis of the crystal and close to its surface are easily frozen onto the surface, since the kinetic forces due to the jerking of the network, and

tending to pull them away from the crystal, are small. Segments which, on the average, lie crosswise to the fiber axis of the crystal, or far from its surface, may also become aligned with the fiber axis and attached to the crystal. These molecular segments will be subject to relatively large kinetic forces tending to tear them out of the crystal; only when the temperature is reduced, and with it the kinetic forces, will they have a good chance of remaining as part of the crystal.

Freezing Conditions

For a given position of a crystal, and given structure of the network, one can then define a freezing temperature characteristic of each surrounding segment of the network—the temperature at which there will be equal probability of finding that segment in the liquid, or frozen to the crystal surface. As thus defined, the freezing point of a segment will be high if it tends to lie parallel to the fiber axis and close to the crystal, and low if it tends to lie crosswise to the fiber axis or farther from the crystal.

Now when a crystal nucleus is formed there will be in its neighborhood molecular segments with a wide variety of freezing points, some below the existing temperature of the material, some above. Whenever a segment with melting point above that of the crystallite comes into contact with it, it will tend to adhere. Thus each crystal will be built up from chain segments with *all possible melting points above the existing temperature*, built into the crystal in more or less random order. In par-

tical, segments with relatively low melting point, subject to relatively large forces tending to pull them out of the crystal, will be overlaid with segments having higher melting points, and will thus be more firmly bound into the crystal. It is thus clear that the rubber crystallites will be formed from non-equivalent chains, and that different crystallites, or parts of crystallites, will be subject to different disruptive forces. The lower the freezing temperature, the more difference there will be in these stresses. It is as though the crystals were formed from inhomogeneous material, with the inhomogeneity greater the lower the freezing temperature.

Melting

We are now in a position to understand the behavior of rubber on melting.

(1) As the temperature is raised, the disruptive forces on the crystallites will increase. Little melting will take place, however, until the temperature is well above the freezing temperature, since the least firmly bound chains, with the lowest melting points, will be overlaid with more strongly adhering ones.

(2) Melting will take place over a range of temperatures, larger and larger parts of the crystallites being disrupted as the temperature increases. The melting range will be broader the more inhomogeneous the material—that is, the lower the temperature at which the rubber was frozen.

(3) The temperature of essentially complete melting will fall gradually with decrease of the freezing temperature, because even the last crystal fragments, made up mostly of chains

with high melting point, will contain a few chains with low melting point which tend to pull them apart.

It will be noted that these predictions of the theory do not depend on the degree to which crystallization has been allowed to proceed. I mention this particularly because the observation that the degree of crystallization does not affect this behavior of rubber has been in conflict with all previous theories.

The melting point of frozen rubber tends to rise as time goes on because the arrangement of molecules into crystals is not absolutely static. From time to time chain segments subject to greater-than-average forces will be detached from the crystal surfaces. These may return to positions on the same crystal, or attach themselves to some other crystal—most probably to the crystal with respect to which they have the highest melting point, since this is the crystal they are most likely to be near. This process leads to a gradual sorting-out of the molecular segments, each going into a crystal position where it will be subject only to small disruptive forces. Thus as time goes on the crystals approach a condition of essential homogeneity and relative freedom from stresses; the melting-point rises and becomes more sharply defined.

It remains to explain the melting behavior of stretched rubber. Stretching of rubber tends to align the molecular segments with the fiber axes of the crystallites, and thus to reduce the freezing temperature of the segments. The more violent the stretching the greater will be this lowering of freezing temperature, and the

greater will be the number of segments which might freeze to a given crystallite at a given temperature. Thus high extension, like low freezing temperature, favors the formation of crystallites subject to large disruptive forces when the material is not stretched, and leads to a lower melting temperature.

No one can tell what may be the practical, technical consequences of these ideas, or of those presented by the preceding speakers. Purely scientific investigations of this type have their greatest effect on technical progress by improving our general understanding of the nature of technical problems. As little as fifteen years ago it was seriously argued (though not generally believed) that the pecu-

liar properties of rubber were due to some mysterious chemical constituent; the rubber chemist of today can work more efficiently because he has a clearer idea of the structure of the substance he wants to produce. Ten years ago the form of the stress-strain curve of rubber was known, of course, but the origin of its peculiarities had been little investigated, and was completely misunderstood. Only as our ideas about the relation between the structure and behavior of materials becomes clear and correct can we hope to design and produce special synthetic materials for special uses, with the directness and efficiency of an architect designing a building to meet special needs.

Women Urged to Study Industry

► IN A RECENT study of opportunities for women chemists, knowledge of engineering subjects was recommended. A director of research of a large foods company advised:

Teach them what industry requires. Those from small colleges especially have no idea of industrial processes or what industry is about.

Another aspect of this gulf between college training and the job in industry or Government is illustrated by a placement director who reported difficulty in placing in industry young women graduating with the bachelor's degree in chemistry who want to do research but don't want to do factory or routine work first. She noted, however, that those who have had contact with industry have a different attitude.

A girl, for example, whose uncle was director of research in an oil company willingly started on a calculating job as part of the learning process. Obviously, visits to the type of laboratory in which one may wish some day to work, talks with women chemists, and, better still, some actual work experience in various types of chemist-employing establishments will help to bridge the gap between textbooks and practice that the engineer is compelled to bridge to qualify for his engineering degree. A few laboratories employ women during the summer months when vacations temporarily reduce their regular staff, offering an opportunity for a try-out both to the college women and the firm.

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